

Chapter 2: A Comparison of the Optical Limiting Properties of Different Single-Walled Carbon Nanotube/Conjugated Polymer Dispersions

Chapter Summary

The effect of the type of polymer used to disperse Single-Walled Carbon Nanotubes (SWNTs) on the optical limiting performances of the resulting dispersions was studied. One conjugated polymer Poly(9,9-di-n-hexylfluorenyl-2,7-diyl) (PFO) possessing a flexible backbone, and two conjugated polymers Poly(2,5-dioctylphenylene-1,4-ethynylene) (PPE), and Poly(9,9-dioctylfluorenyl-2,7-yleneethynylene) (PFE) possessing rigid backbones were used to disperse the SWNTs. It was found that the resulting optical limiting performances depended on the structure (rigid or flexible) of the polymers, as well as on the number of aromatic groups present in the backbone of the rigid conjugated polymers.

2.1 Introduction

In recent years, a significant number of studies have been performed on the nonlinear optical properties of carbon structures. Carbon black suspensions have been studied as potential optical limiting materials¹⁻⁴. More recently, multi-walled and single-walled carbon nanotubes have been demonstrated to be efficient optical limiters⁵⁻¹⁰. Izard et al.¹¹ and Jin et al.¹² demonstrated that the diameter of SWNTs dispersed in a solvent played a major role in the optical limiting properties of the dispersion. It may thus be assumed that using polymers interacting differently with SWNTs and giving different SWNT diameter distributions would give different optical limiting properties. In this study, the effect played by the type of polymer used to disperse SWNTs was studied. More specifically polymers with flexible and rigid aromatic backbones were used. A number of studies were performed which showed that a flexible polymer soluble in a certain solvent could render SWNTs soluble in that same solvent by wrapping itself around the nanotubes¹³⁻¹⁵. Chen et al.¹⁶ demonstrated that π - π interactions were involved

in the dispersion of SWNTs with rigid polymers containing aromatic groups. They showed that smaller diameter nanotubes could be dispersed with a rigid conjugated polymer when compared to a flexible one and that depending on the type of SWNTs used, nano-ribbon assemblies were formed due to π - π interaction between the aromatic groups composing the backbone of the rigid polymer molecules and the SWNTs. Nano-ribbons present in the structure are expected to induce stronger optical limiting properties due to the larger diameters associated with bundles of SWNTs when compared to individual SWNTs. It is thus of interest to study the influence of the type of polymer used to disperse SWNTs on the resulting nonlinear optical properties, especially considering that rigid conjugated polymers give more stable dispersions than flexible ones due to the irreversible interaction existing between a rigid conjugated polymer backbone and a nanotube through π -stacking. The strong attraction between a SWNT and a rigid conjugated polymer was attributed to the fact that the atomic arrangement of carbon atoms in an aromatic group is similar to their arrangement on the surface of a SWNT¹⁶⁻¹⁹.

In this chapter, three different conjugated polymers were used to disperse purified SWNTs in chloroform. The optical limiting performances of SWNTs dispersed with a flexible conjugated polymer were compared to the optical limiting performances of SWNTs dispersed with two different rigid conjugated polymers. The results obtained were explained in terms of differences in the diameters of the SWNTs, which were related to the type of polymer, which was used to disperse the SWNTs.

2.2 Experimental Section

2.2.1 Materials

Raw Single-Walled Carbon Nanotubes produced by Chemical Vapor Deposition (CVD) were obtained from Optics Innovations Inc. The SWNTs were purified according to a method developed by Chiang et al.²⁰. Raw SWNTs were heated in air in a tube furnace for 18h at 225°C. The oxidized SWNTs were sonicated in concentrated hydrochloric acid for 15 min with 0.1g of SWNTs per 100mL of acid. The resulting

dispersion was centrifuged at 2500 rpm for 20 min, and the acidic supernatant removed. The remaining SWNTs were filtered and rinsed several times with de-ionized water until the pH of the filtrate became neutral to eliminate any remaining traces of acid. The deionized water was obtained from an 18 MΩ-cm Barnstead water system. The resulting soot was further oxidized at 325°C for 1h30 min, and the same centrifugation, filtration and rinsing steps as previously described were applied.

Poly(9,9-di-n-hexylfluorenyl-2,7-diyl) (PFO), Poly(2,5-dioctylphenylene-1,4-ethynylene) (PPE), and Poly(9,9-dioctylfluorenyl-2,7-yleneethynylene) (PFE) were purchased from Sigma-Aldrich. The structures of the three polymers are represented in Figure 2.1. The molecular weights (Mw) of the polymers were determined by Size Exclusion Chromatography (SEC) and were 17 400g/mol, 37 760g/mol, =10190g/mol for PFO, PPE, and PFE respectively.

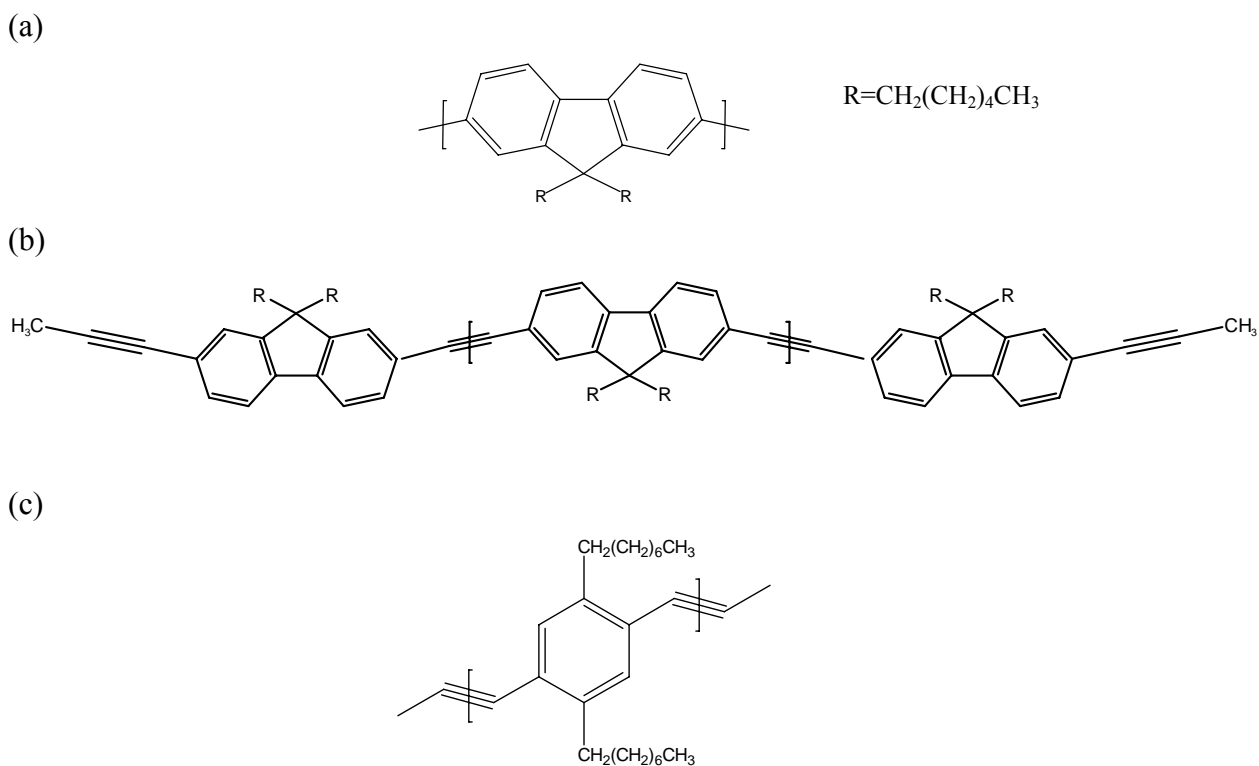


Figure 2.1. Structure of (a) PFO, (b) PFE, and (c) PPE.

Solutions of SWNTs and polymers were obtained by mixing 0.005g of SWNTs with solutions of 0.005g of polymer per 10 mL of chloroform. The resulting mixtures were sonicated for 30 min and left undisturbed for several days. The linear transmittances of each SWNT/conjugated polymer dispersion was adjusted to 70% by mixing an appropriate amount of the corresponding pure polymer solution with the stable SWNT/polymer dispersion, and the optical limiting performances of the resulting samples were measured.

2.2.2 Characterization and Optical Measurements

Size Exclusion Chromatography (SEC) was used to determine the molecular weights of the polymers with a Waters 717 auto-sampler, Waters 2410 refractive index detector, a Wyatt Technology mini-DAWN triple-angle light scattering detector, and a Viscotek viscometer. The solvent used was chloroform at a flow rate of 1mL/min.

A Philips 420 T Transmission Electron Micrograph (TEM) was used to visualize the SWNTs dispersed with the different polymers. The TEM samples were prepared by drying a drop of SWNT/polymer solution on a Lacey Carbon TEM grid (200 mesh), followed by rinsing with pure chloroform to eliminate excess polymer, which enabled us to visualize the dispersed SWNTs. A Digital Instruments Nanoscope IIIa Atomic Force Microscope (AFM) in the tapping mode was utilized to estimate the diameters of the nanotubes in the different dispersions based on height images.

Fluorescence measurements of all solutions and composites were carried out with a Hitachi-F-4500 spectrofluorimeter. Transmission spectra were recorded with a Shimadzu UV-2501 PC spectrophotometer. Thermogravimetric analysis of the samples was carried out on a Q500 Texas Instrument thermogravimetric analyzer.

The nonlinear optical experiments were performed using a Ti:Sapphire laser operating at 800 nm, with a 75.8 MHz pulse repetition rate and a 200fs pulse width. The dispersions were contained in 2mm quartz cells.

2.3 Results and Discussion

The raw SWNTs were thoroughly purified in order to reduce as much as possible the amount of impurities present in the soot used to prepare the SWNT/conjugated polymer solutions. This was performed in order to ensure that the scattering of light responsible for the optical limiting effects would as much as possible be related to the SWNTs and not combined to the scattering of other carbon particles as previously observed^{6,7}. Figure 2.2 represents the purified SWNTs used in this study.

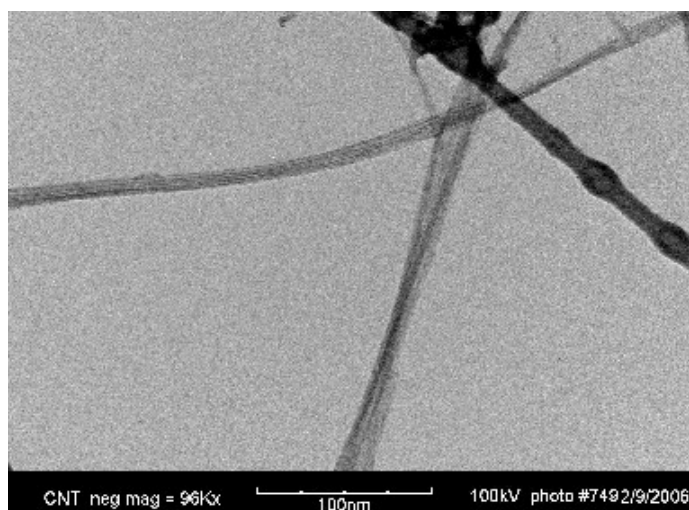


Figure 2.2. Purified SWNTs.

Using solutions of equal transmittances was deemed more appropriate for comparing the nonlinear optical properties of the samples than using dispersions of equal SWNT content. Thermogravimetric analysis (TGA) of the pure polymers and purified SWNTs revealed that the decomposition temperatures of the polymers and the nanotubes were overlapping rendering difficult a precise estimate of the SWNT concentrations inside the dispersions once they were decanted. Likewise, Riggs et al.²¹ used samples of equal linear transmittances to compare the nonlinear optical properties of full and shortened SWNTs dispersed and solubilized in water.

As shown in Figure 2.3, the three conjugated polymers had the same absorbance at 800 nm. Adjusting the transmittance of the polymer/SWNT solutions to 70% (Figure 2.4) ensured to obtain reasonably similar concentrations of SWNTs for the three different

polymer/SWNT dispersions, thus allowing us to compare only the effect of the dispersion of SWNTs by the three different polymers on the resulting optical limiting properties. Furthermore, Riggs et al.²¹ observed that while the concentration had an effect on the optical limiting properties of solutions of SWNTs, it did not have an effect on the optical limiting properties of dispersions of SWNTs of equal linear transmittance, thus implying that for our study the differences observed in the optical limiting properties of the dispersions were mostly related to the differences in dispersion of the SWNTs bundles.

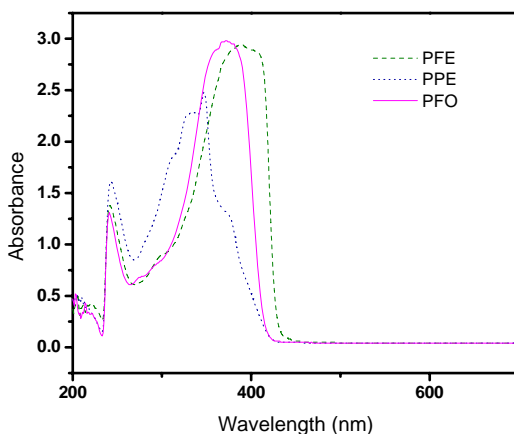


Figure 2.3. Absorbance spectra of the three polymer solutions.

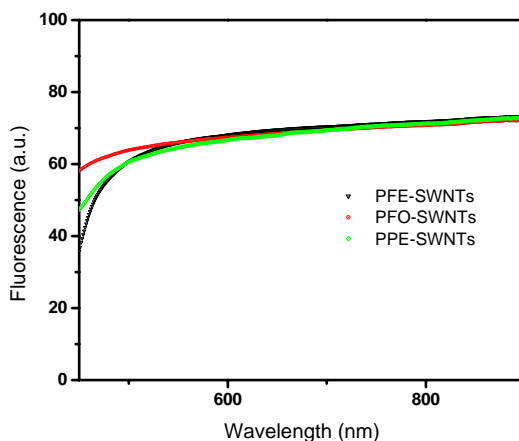


Figure 2.4. Linear transmission spectra of the PFE/SWNTs, PFO/SWNTs, PPE/SWNTs dispersions.

The interactions of the polymers with the purified SWNTs were characterized by fluorescence measurements. Figure 2.5 shows the fluorescence spectra of stable PFO/SWNT, PFE/SWNT, and PPE/SWNT dispersions for equal linear transmittances of 70% along with the fluorescence spectra of pure polymer solutions. It was noticed that in each case, the fluorescence of the polymer was significantly decreased by the presence of SWNTs in the dispersions, which was attributed to the transfer of energy from the polymers to the SWNTs¹⁶. The decrease in fluorescence was similar for the PFE/SWNT and PFO/SWNT dispersions, while it was significantly higher for the PPE/SWNT dispersion. This was attributed to the inherent photochemical instability of PPE, rather than to a stronger interaction of the polymer with the SWNT, the PPE/SWNT dispersions being unstable when compared to the PFE/SWNT and PFO/SWNT dispersions.

Figure 2.6 shows the output laser intensity as a function of the input laser intensity of the pure polymer solutions for a concentration of 0.005g/10mL of chloroform. No decrease in the transmitted energy could be noticed, indicating that the optical limiting effects observed for the SWNT/conjugated polymer solutions in the subsequent experiments were only related to the SWNTs. Figure 2.7 represents the output laser intensity as a function of the input laser intensity for the PFO/SWNT, PFE/SWNT, and PPE/SWNT dispersions for an equal linear transmittance of 70%. For each of the dispersions studied, a significant decrease of the output intensity was noticed, as previously observed for SWNT dispersions^{6,7}. Macroscopic bubbles started to appear around $47\text{MW}\cdot\text{cm}^{-2}$ for all three dispersions. For input intensities lower than $47\text{MW}\cdot\text{cm}^{-2}$, solvent vapor formation was the mechanism responsible for light scattering, while for input intensities higher than $47\text{MW}\cdot\text{cm}^{-2}$, bubble formation was responsible for light scattering.

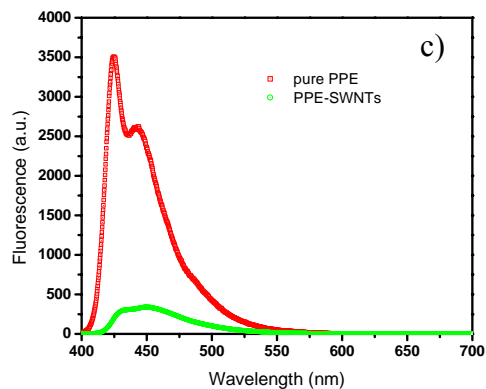
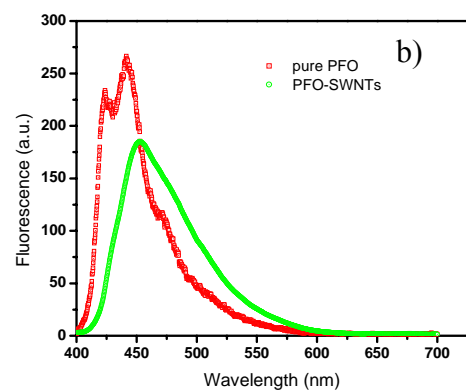
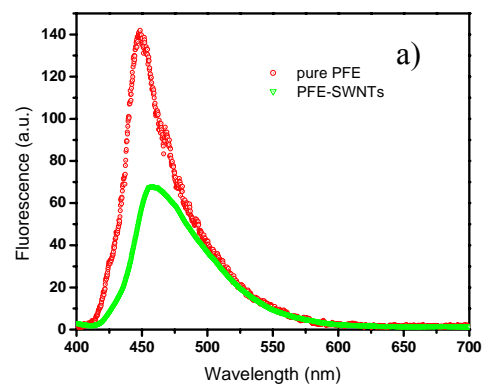


Figure 2.5. Fluorescence spectra of: (a) PFE and PFE/SWNT dispersion, (b) PFO and PFO/SWNT dispersion, and (c) PPE and PPE/SWNT dispersion.

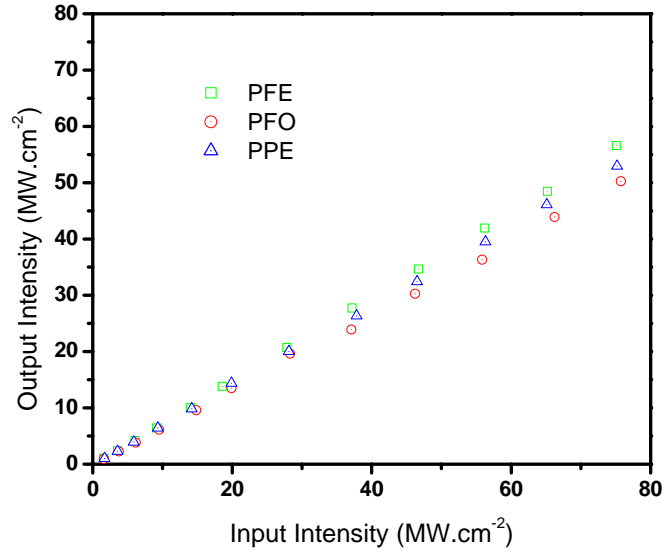


Figure 2.6. Optical limiting performances of the pure polymer solutions.

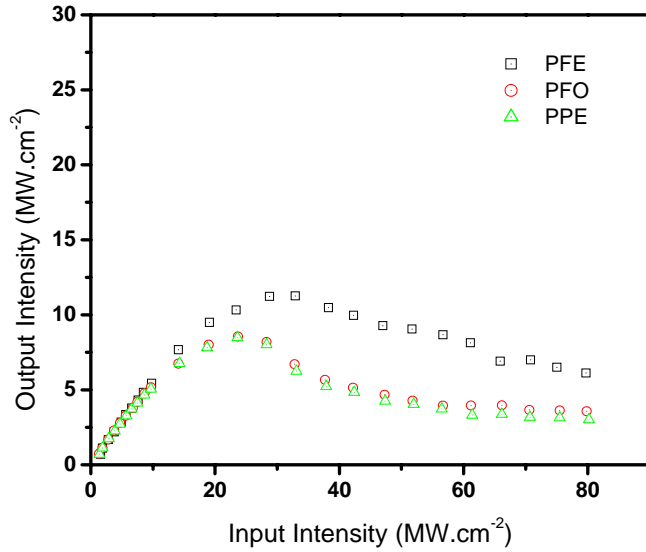


Figure 2.7. Optical limiting performances for the SWNT/polymer dispersions.

The output laser intensity was higher for the PFE/SWNT dispersion than for the PFO/SWNT and PPE/SWNT dispersions. PPE/SWNT dispersions presented the higher optical limiting effects of the three dispersions. The optical limiting thresholds obtained

with PFE/SWNT, PFO/SWNT, and PPE/SWNT samples were approximately 120, 97, and 97 MW.cm⁻². These differences were attributed to the differences existing between the diameters of the bundles of SWNTs in the dispersions. As mentioned in the introduction, conjugated polymers with flexible and rigid backbones disperse SWNTs differently. For SWNTs dispersed with a rigid conjugated polymer, and depending on the type of SWNTs used, Chen et al.¹⁶ obtained dispersions of SWNTs containing either a majority of small diameter nanotubes or dispersions containing a majority of nano-ribbon assemblies. A study of the diameters of the bundles in the different SWNT/polymer dispersions by AFM section analysis based on height images showed that the average diameter of the bundles for the PFE/SWNT dispersion was lower than for the dispersions involving PFO and PPE. An average bundle diameter of 3.391, 5.395, and 5.460 nm was obtained for the PFE/SWNT, PFO/SWNT, and PPE/SWNT dispersion respectively. Furthermore, TEM pictures of the dispersions confirmed that the PFE/SWNT dispersions were in majority composed of smaller diameter SWNT bundles coexisting with a few larger diameter bundles (Figure 2.8). Izard et al.¹¹ demonstrated that bundles of SWNTs with a higher diameter provided better optical limiting properties than bundles of SWNTs with smaller diameters. This difference was attributed to the light scattering mechanisms underlying the optical limiting effects induced by SWNTs, larger diameter bundles providing larger bubble nucleation centers. The smaller diameter of the bundles of SWNTs dispersed with PFE thus gave lower optical limiting performances when compared to the SWNTs dispersed with PFO or PPE. The slightly higher optical limiting performances obtained with the SWNTs dispersed with PPE when compared to SWNTs dispersed with PFO may be explained by the low amount of aromatic groups present in the backbone of PPE, which provided a decreased interaction between the polymer and the SWNT surface when compared to a rigid polymer containing several aromatic groups like PFE, thus hindering the dispersion of the SWNTs in the polymer solution, which gave higher bundle diameter. This was confirmed by the higher instability of the PPE/SWNTs dispersion when compared to the PFE/SWNT and PFO/SWNT dispersions.

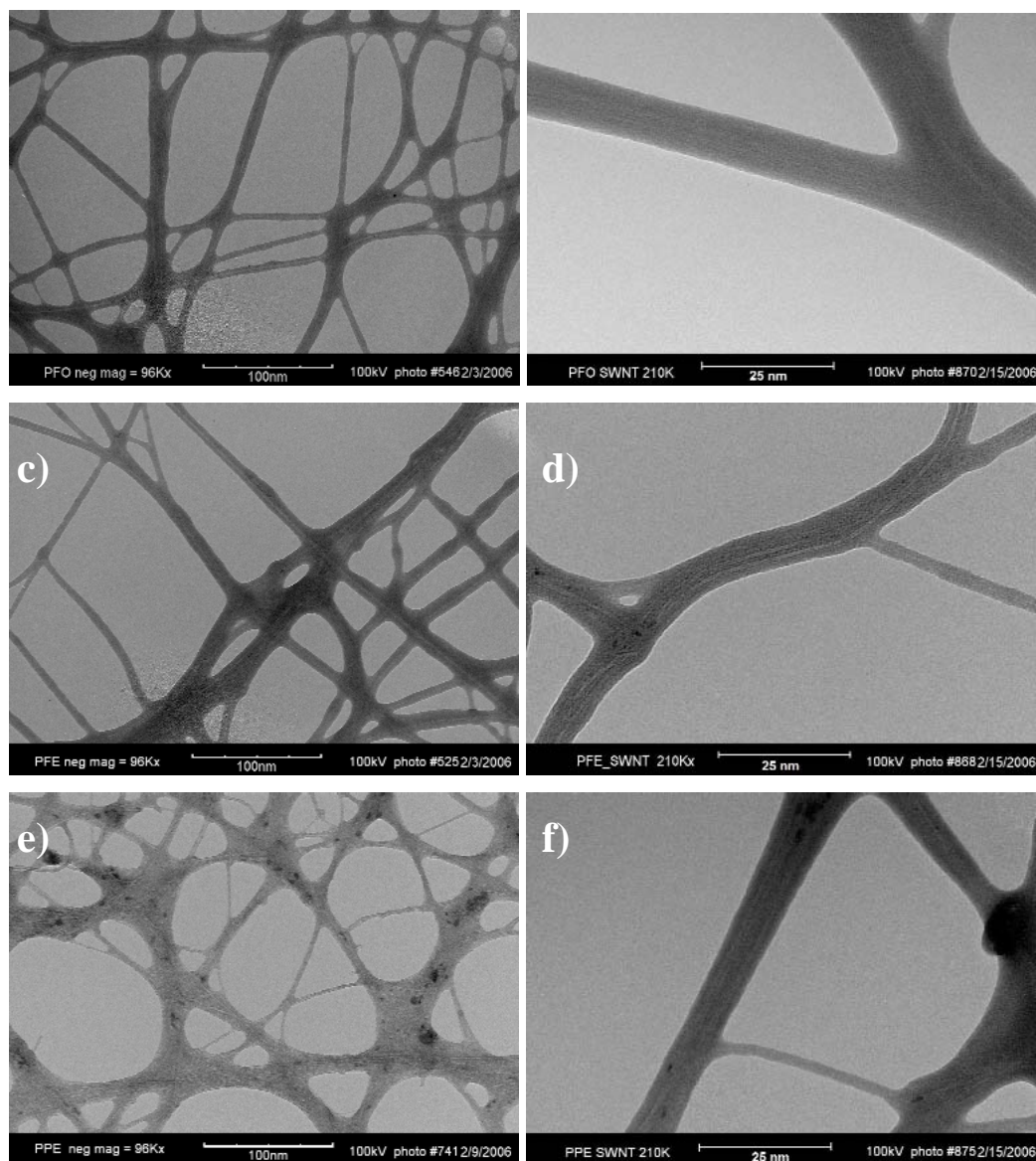


Figure 2.8. Transmission Electron Micrographs of: (a) and (b) PFO/SWNT dispersion. (c) and (d) PFE/SWNT dispersion. (e) and (f) PPE/SWNT dispersion.

2.4 Conclusions

Three different conjugated polymers, PFO, PFE, and PPE, differing by their structure were used to disperse purified SWNTs in chloroform. Higher optical limiting performances were obtained for the PFO/SWNT and PPE/SWNT dispersions. This was attributed to the larger diameter of the SWNT bundles present in the PFO/SWNT and

PPE/SWNT dispersions, when compared to the diameter of the SWNT bundles present in the PFE/SWNT dispersion. The smaller diameters of the SWNT bundles in the PFE/SWNT was attributed to the π - π interactions existing between the aromatic groups of the rigid backbone of PFE and the hexagonal carbon atom network present on the surface of the SWNTs.

2.5 References

- (1) Mansour, K., Soileau, M. J., and Van Stryland, E. W. *Journal of the Optical Society of America B* **1992**, *9*, 1100.
- (2) Nashold, K. M., and Walter, D. P. *Journal of the Optical Society of America B* **1995**, *12*, 1228.
- (3) Goedert, R., Becker, R., Clements, A., and Whittaker III, T. *Journal of the Optical Society of America B* **1998**, *15*, 1442.
- (4) Vincent, D., Petit, S., Chin, S. L. *Applied Optics* **2002**, *41*, 2944-2946.
- (5) Sun, X., Yu, R. Q., Xu, G. Q., Hor, T. S. A., and Ji, W. *Applied Physics Letters* **1998**, *73*, 3632-3634.
- (6) O'Flaherty, S. M., Hold, S. V., Brennan, m. E., Cadek, M., Drury, A., Coleman, J. N., and Blau, W. J. *Journal of the Optical Society of America B* **2003**, *20*, 49-58.
- (7) O'Flaherty, S. M., Murphy, R., Hold, S. V., Cadek, M., Coleman, J. N., and Blau, W. J. *Journal of Physical Chemistry B* **2003**, *107*, 958-964.
- (8) Kataura, H., Kumazawa, Y., Maniwa, Y., Umezue, I., Suzuki, S., Ohtsuka, Y., and Achiba, Y. *Synthetic Metals* **1999**, *103*, 2555-2558.
- (9) Vivien, L., Riehl, D., Anglaret, E., and Hache, F. *IEEE Journal of Quantum Electronics* **2000**, *36*, 680-686.
- (10) Vivien, L., Anglaret, E., Riehl, D., Hache, F., Bacou, F., Andrieux, M., Lafonta, F., Journet, C., Goze, C., Brunet, M., and Bernier, P. *Optics Communications* **2000**, *174*, 271-275.
- (11) Izard, N., Billaud, P., Riehl, D., and Anglaret, E. *Optics Letters* **2005**, *30*, 1509-1511.

- (12) Jin, Z., Huang, L., Goh, S. H., Xu, G., and Ji, W. *Chemical Physics Letters* **2002**, 352, 328-333.
- (13) Star, A., Stoddart, J. F., Steuermann, D. W., Diehl, M., Boukai, A., Wong, E. W., Yang, X., Chung, S.-W., Choi, H., and Heath, J. R. *Angewandte Chemie, International Edition* **2001**, 113, 1771-1775.
- (14) O'Connell, M., Boul, P., Ericson, L. M., Huffman, C., Wang, Y., Haroz, E., Kuper, C., Tour, J., Ausman, K. D., Smalley, R. E. *Chemical Physics Letters* **2001**, 342, 265-271.
- (15) Wang, J., Musameh, M., and Lin, Y. *Journal of the American Chemical Society* **2003**, 125, 2408-2409.
- (16) Chen, J., Liu, H., Weimer, W. A., Halls, M. D., Waldeck, D. H., and Walker, G. C. *Journal of the American Chemical Society* **2002**, 124, 9034-9035.
- (17) Jaegfeldt, H., Kuwana, T., and Johansson, G. *Journal of the American Chemical Society* **1983**, 105, 1805.
- (18) Katz, E. *Journal of electroanalytical Chemistry* **1994**, 357, 157.
- (19) Chen, R. J., Zhang, Y., Wang, D., and Dai, H. *Journal of the American Chemical Society* **2001**, 123, 3838-3839.
- (20) Chiang, I. W., Brinson, B. E., Huang, A. Y., Willis, P. A., Bronikowski, M. J., Margrave, J. L., Smalley, R. E., and Hauge, R. H. *Journal of Physical Chemistry B* **2001**, 105, 8297-8301.
- (21) Riggs, J. E., Walker, D. B., Carroll, D. L., and Sun, Y-P. *Journal of Physical Chemistry B* **2000**, 104, 7071-7076.