



Article Chromatic Conductive Polymer Nanocomposites of Poly (p-Phenylene Ethynylene)s and Single-Walled Carbon Nanotubes

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Abstract: We report on dispersions and thin films of chromatic conductive nanocomposites of poly(*p*-phenylene ethynylene)s (PPEs) and single-walled carbon nanotubes (SWNTs) generated via solution mixing. The linear, conjugated PPEs with dialkyl- and dialkyloxy-side chain groups are shown to debundle and disperse high concentration (up to 2.5 mg/mL) SWNTs in various organic solvents. The solubilization of SWNTs and PPE wrapping is accompanied with the change in the solution color. Ultraviolet visible absorption spectra of nanocomposite solutions demonstrate a new absorption peak at a higher wavelength, supporting the observed chromatism. Fluorescence spectra of nanocomposite solutions display significant quenching of the fluorescence intensity and the Stern-Volmer model is used to analyze fluorescence quenching. Electron microscopy of the chromatic solid films of high mass fraction PPE/SWNT nanocomposites obtained by vacuum filtration reveals the debundled SWNTs in the PPE matrix. The tensile strength and Young's modulus of these PPE/SWNT nanocomposite films are as high as 150 MPa and 15 GPa, respectively. The composite films exhibit remarkably high conductivities, ranging from ~1000 S/m to ~10,000 S/m for 10 wt% and 60 wt% SWNT nanocomposites, respectively.

Keywords: conductive polymer nanocomposites; carbon nanotubes; conjugated polymers; chromatic materials

1. Introduction

Single-walled carbon nanotubes (SWNTs) are promising for various potential applications such as electronic and biomedical devices and advanced conductive composite materials because of their unique 1D nanostructure, excellent electrical conductivities and mechanical properties [1–5]. However, processing difficulties limit the realization of their full potential because SWNTs readily form bundles, which derive from strong van der Waals attractions between nanotubes. Several methods including chemical surfacefunctionalization and molecular physical interactions have been successfully developed to increase repulsive inter-tube interactions in order to disperse SWNTs down to the individual tubes. These methods include acid oxidation, [6] covalent functionalization, [7] surfactant adsorption, [8] and polymer wrapping [9]. The latter is the focus of this work, which has the advantage that conductive polymer nanocomposites can potentially be produced directly by vacuum filtration from a solution without altering the chemical structures of the pristine SWNTs.



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Conjugated polymers are organic semiconductors, which are extensively used in the fabrication of organic electronic devices such as solar cells, light-emitting diodes, sensors and field-effect transistors [10–12]. It has been recognized that the π -conjugated backbone of conjugated polymers strongly interacts with the π -electron surface of SWNTs and solubilizing alkyl side chains of conjugated polymers enables exfoliation and dispersion of the SWNTs in organic solvents [9]. Highly concentrated SWNT dispersions (>1 mg/mL) in common organic solvents have been reported when using poly(3-alkyl thiophene)s (P3AT), [13] poly(arylene ethynylene)s (PAEs), [14] poly(9,9'-diakylfluorene)s (PFx), [9] and poly(phenylene vinylene)s (PPVs) [15]. The resulting conductive polymer nanocomposites exhibit synergistic optoelectronic effects. The combination of conjugated polymers and SWNTs can dramatically improve the electrical conductivities and charge mobilities [16–18]. It has been shown that SWNT-based conductive polymer composites as device active layers can efficiently improve the overall efficiency of photovoltaic cells [19–21] and device performance of field effect transistors [22–24].

Poly(*p*-phenylene ethynylene)s (PPEs) are a fascinating class of linear conjugated polymers with rigid backbone conformation [25–27]. PPEs are sensitive to their surroundings, including changing their color due to torsion-dependent modulation of their electronic properties, with strong thermo- and solvatochromic behavior observed in the dialkyl-PPEs and dialkyloxy-PPEs [27–29]. It is thought that planarization of the linear conjugated backbone is responsible for the unusual optical properties [29]. PPEs have been used to solubilize SWNTs in various organic solvents [30–32]. The rigid, linear-shaped backbone conformation of the PPEs has shown unique effectiveness in exfoliating SWNTs down to individual tubes. For instance, complete dispersion in chloroform up to 2.2 mg/mL SWNT has been reported [33]. The PPEs are highly chromatic materials; however, to the best of our knowledge, there are no reports of chromatic materials of PPE/SWNT nanocomposites to date.

In this work, we report chromatic PPE/SWNT nanocomposites generated via simple solution mixing. The significant change in the solution color occurs when the SWNTs are debundled and dispersed in the organic solvents due to PPE wrapping. Absorption and emission spectra of dispersions are analyzed to explain such chromatism. After vacuum filtration, high mass fraction PPE/SWNT nanocomposites are obtained and they exhibit excellent mechanical performance and extremely high electrical conductivities.

2. Materials and Methods

The SWNTs (Cheap Tubes Inc., Cambridgeport, VT, U.S.A.) were used as received without further treatment. The SWNTs had average diameters of around 1–2 nm. Two kinds of PPEs with dialkyl and dialkyloxy side chain groups were studied and their chemical structures are shown in Scheme 1. Mixtures of SWNTs and PPEs were sonicated in organic solvents (chloroform, dichlorobenzene (DCB) or toluene) with a typical solid concentration of 4.0 mg/mL for 30 min to generate stable dispersions. The mass ratio of SWNTs and PPEs was varied from 0.625:100 to 60:40. The SWNT/PPE dispersions were then dropped into the methanol and the thin films of nanocomposites were obtained by vacuum filtration. The resulting films were dried at room temperature under a vacuum and then they were peeled off from the filter paper for further investigation.

UV-vis absorption and fluorescence spectra of the solutions were acquired using a Shimadzu UV02401PC spectrophotometer and a PTI LPS-220B spectrofluorophotometer, respectively. The morphology of the solid films was examined with scanning electron microscopy (SEM, LEO 1530) operating at an accelerating voltage of 5 kV. The mechanical properties of the composite films cut to give a gauge width of 10 mm were determined using an RSA III solids analyzer (Rheometric Scientific, Co., Piscataway, NJ, U.S.A.) at room temperature at a strain rate of 0.05 mm/min. The electrical conductivities of nanocomposite films were conducted on a Keithley Instrument 2000 Source Meter in a four-point probe configuration and the specimen thickness was measured by a digital caliper (VWP).



PPEC8: R₁=R₂=C₈C₁₇; n=136 PPEOC8: R₁=R₂=OC₈C₁₇; n=45

Scheme 1. Chemical structures of poly(*p*-phenylene ethynylene)s (PPEs). Dioctyl-PPE denoted as PPEC8 has 136 repeated units while dioctyloxy-PPE denoted as PPEOC8 has 45 repeated units.

3. Results

3.1. Chromatic Dispersion of SWNT-PPE Nanocomposites

The solubilities of SWNTs in various organic solvents utilizing PPEC8 and PPEOC8 in 1:1 mass ratios with the SWNT are shown in Table 1. The organic solvents used (odichlorobenzene (DCB), chloroform and toluene) were selected as they are good solvents for PPEs. Although SWNTs are insoluble in chloroform and toluene, and only weakly dispersible in DCB, they became highly soluble when added to the PPE solutions. The dispersions of SWNTs/PPE remained fully homogeneous without any signs of separation or precipitation for several weeks after mixing. This observation confirms PPEs act as good dispersing agents for solubilizing SWNTs in organic solvents [14]. The higher dispersion concentration of SWNTs observed with PPEC8 compared with PPEOC8, demonstrates that SWNTs have stronger interactions with the PPEC8. This phenomenon is believed to be attributed to a higher degree of polymerization of the PPEC8 [34]. The higher degree of polymerization of PPEC8 produces a longer conjugated backbone and consequently larger contacts per chain with nanotubes via π - π interactions. The highest SWNT dispersion concentrations of ~2.5 mg/mL are obtained with PPEC8 in DCB. This value can be favorably compared to the previously reported values of 2.2 mg/mL of SWNTs with PPEs in chloroform [33] and 2.75 mg/mL of SNWTs with P3ATs in DCB [13]. As may be expected, higher concentration SWNT/PPE solutions have higher viscosities in DCB; however, the SWNT/PPE dispersions in this work did not form a gel in contrast to the literature report [35].

Table 1. Maximum solubility (mg/mL) of SWNTs in various solvents by PPE wrapping ^(a).

Polymer	DCB	Chloroform	Toluene
PPEC8	2.5	2.2	0.5
PPEOC8	1.5	1.5	0.3

^(a) The mass ratio of SWNTs to PPE was set to be 1:1.

As a consequence of solubilization of the SWNTs by PPE wrapping, we observed a simultaneous color change in the PPE solution. Figure 1 shows the color change of PPEs in DCB by adding various amounts of SWNTs. The starting PPE solution concentration is set as 1 mg/mL. Adding 0.625 wt% SWNTs (relative to PPE amount) into the PPE solution results in color changes from yellow to blue–yellow for PPEC8 (Figure 1a) and from orange to green–orange for PPEOC8 (Figure 1b). With increasing SWNT loading, the chromatic solutions become darker. A similar chromatic behavior has been reported in the PPV/SWNT nanocomposites [15]. The color change is attributed to the conformation change of the conjugated backbone as a result of interaction with SWNTs [15]. It is well known that nanotubes can act as a template for polymer orientation across nanotube–polymer interfaces [36–38]. At a molecular level, the polymer chains are aligned along the tube long axis, forming an ordered interfacial polymer structure on nanotube surfaces [39,40]. In the conjugated polymers, this ordered polymer structure yields the extended π -electron delo-

calization [33]. As such the nanotubes act as a doping agent for enhancing the stabilization of the excited states of conjugated polymers, resulting in a drastic change in the solution color [15].



Figure 1. Images of (**a**) PPEC8/SWNT and (**b**) PPEOC8/SWNT nanocomposites in DCB. In each image, SWNT loading relative to PPE amount in the vials from left to right is 0 wt%, 0.625 wt%, 1.25 wt%, 2.5 wt%, 5 wt% and 10 wt%. The PPE concentration is set as 1 mg/mL.

The SWNT doping of PPE is further confirmed by the optical properties. Typically, the PPE/SWNT nanocomposites in DCB were diluted 30 times for investigation of optical properties. Figure 2 shows the UV-Vis absorption spectral features of PPEC/SWNT and PPEOC8/SWNT nanocomposites in DCB with different SWNT loading. Pure PPEC8 and PPEOC8 show a broad absorption band of π -conjugation centered at λ ~400 nm and λ ~450 nm, respectively. Adding SWNTs into the PPE solution produced a significant change in the intensity of the π -conjugation band as well as appearance and increase in intensity of a new absorption band at a higher wavelength. The new absorption band is located at λ ~450 nm and λ ~510 nm for PPEC8/SWNT and PPEOC8/SWNT, respectively. Appearance of new absorption bands at a higher wavelength in the PPE solution upon adding SWNTs indicates SWNT doping of PPE via π - π interactions between PPE backbones and SWNTs, producing the change in the solution color. This observation is in good agreement with the literature report on the PPV/SWNT nanocomposites in chloroform [15].



Figure 2. UV-Vis solution spectra of (**a**) PPEC8/SWNT and (**b**) PPEOC8/SWNT in DCB. The SWNT loading relative to PPE amount is 0 wt%, 0.625 wt%, 1.25 wt%, 2.5 wt%, 5 wt% and 10 wt%. The PPE concentration is set as 1 mg/30 mL.

Figure 3 shows fluorescence spectral features of PPEC8/SWNT and PPEOC8/SWNT nanocomposites in DCB as well as control polymers PPEC8 and PPEOC8. Apparently, the addition of SWNTs to PPE solutions results in the quenching of PPE fluorescence for

both PPEC8 and PPEOC8. The decrease in PPE fluorescence intensity with increasing SWNTs is attributed to a decreased quantity of free PPE fluorophore. This fluorescence quenching of PPE/SWNT nanocomposites is believed to be caused by energy transfer from the PPE-conjugated backbone as an energy donor to the SWNTs as an energy acceptor, indicating that PPE/SWNT nanocomposites involve strong π - π interactions between PPE-conjugated backbones and SWNTs in DCB [41]. This observation is in good agreement with the literature reports on PPE/SWNT nanocomposites. [42,43].



Figure 3. Fluorescence spectra (excitation at $\lambda = 350$ nm) of (**a**) PPEC8/SWNT and (**b**) PPEOC8/SWNT in DCB. The SWNT loading relative to PPE amount is 0 wt%, 0.625 wt%, 1.25 wt%, 2.5 wt%, 5 wt% and 10 wt%. The PPE concentration is set as 1 mg/30 mL.

Figure 4 shows changes of the fluorescence intensity of PPE versus SWNT concentration for PPEC8/SWNT and PPEOC8/SWNT in DCB. According to the Stern–Volmer model, [41] the fluorescence intensity *I* is express by $(I_0 - I)/I = k_{SV} [Q]$, where I_0 is the intensity without SWNTs, k_{SV} is a Stern–Volmer interaction parameter, and [Q] is the concentration of the quencher (in this case the concentration of the SWNT). Linear fits to the fluorescence data using the Stern–Volmer model gives a k_{SV} ~490 mL/mg for PPEC8/SWNT nanocomposites and a k_{SV} ~147 mL/mg for PPEOC8/SWNT nanocomposites. The larger k_{SV} for the PPEC8/SWNT than that in PPEOC8/SWNT may be attributed to the larger degree of polymerization in PPEC8/SWNT (n = 136) than that in PPEOC8/SWNT (n = 45). These results indicate that the SWNTs have stronger π - π interactions with PPEC8 than that with PPEOC8. This observation is consistent with the SWNT solubility (Table 1) and optical absorption data (Figure 2).



Figure 4. Stern–Volmer plots of change of fluorescence intensity versus SWNT concentration. (**a**) PPEC8-SWNT and (**b**) PPEOC8-SWNT.

3.2. Chromatic Nanocomposites of PPE/SWNT

High mass fraction PPE/SWNT nanocomposite films were received via vacuum filtration. The materials were mechanically robust and folding them 10 times resulted in no obvious mechanical damage. Figure 5 shows typical photographs of chromatic films of PPE/SWNT nanocomposites with 50 wt% SWNTs. Apparently, PPEC8/SWNT nanocomposite films are purple–blue while PPEOC8/SWNT nanocomposite films are green. We prepared various PPE/SWNT nanocomposites with SWNT loading in the range between 10 and 60 wt%. With increasing SWNT loading, the chromatic PPE/SWNT nanocomposites became darker.



Figure 5. Photographs of chromatic nanocomposites with 50 wt% SWNTs. (**a**) PPEC8/SWNT and (**b**) PPEOC8/SWNT.

Figure 6 shows typical SEM images of the PPEC8/SWNT and PPEOC8/SWNT nanocomposites containing 50 wt% SWNTs. We can see that the entangled SWNTs and bundles are shown as nanofibrils. The SWNTs are seen to be homogeneously dispersed in the PPE matrix with no significant aggregations observed in either the PPEC8/SWNT or PPEOC8/SWNT nanocomposites. This morphology supports that SWNTs are debundled by PPE wrapping, which is in good agreement with solubility data and optical absorption/fluorescence spectra as discussed above.



Figure 6. Typical scanning electron micrographs of PPE/SWNT nanocomposites containing 50 wt% SWNTs. (a) PPEC8/SWNT and (b) PPEOC8/SWNT. The SWNTs are shown as entangled nanofibrils in the polymer matrix.

The mechanical performance of high mass fraction PPE/SWNT nanocomposites was quantified by tensile testing. Figure 7 shows typical stress–strain curves of PPEC8/SWNT

and PPEOC8/SWNT nanocomposite films with various nanotube loading of 10–60 wt%. The tensile strength is, respectively, 100–150 MPa and 25–80 MPa for PPEC8/SWNT and PPEOC8/SWNT while the Young's modulus is, respectively, 9–15 GPa and 2–10 GPa for PPEC8/SWNT and PPEOC8/SWNT (see Figure 8). PPEC8 possesses 136 repeated units which is three times the repeated units (n = 45) in PPEOC8. The longer conjugated backbone of PPEC8 yields stronger π - π -interaction between PPE and SWNTs and thereafter the more efficient load transfer from PPE to SWNTs.



Figure 7. Stress–strain curves of the PPE/SWNT nanocomposites with various SWNT loadings. (**a**) PPEC8/SWNT and (**b**) PPEOC8/SWNT. The SWNT loading is shown in the plots.



Figure 8. Mechanical properties of the PPE/SWNT nanocomposites versus SWNT loading. (**a**) Tensile stress and (**b**) Young's modulus.

The strength and Young's modulus of both PPEC8/SWNT and PPEOC8/SWNT nanocomposites increase more or less linearly with increasing SWNT loading. These results are generally associated with good load transfer from the polymer matrix to the SWNTs [44]. The slope of the strength versus SWNT loading curve is, respectively, 300 MPa and 128 MPa for PPEC8/SWNT and PPEOC8/SWNT, while the slope of Young's modulus versus SWNT loading curve is, respectively, 32 GPa and 14 GPa for PPEC8/SWNT and PPEOC8/SWNT. The data further confirm that the PPEC8 is more effectively reinforced by SWNTs than the PPEOC8.

The DC electrical conductivity of chromatic PPE/SWNT nanocomposites (see Figure 9) shows that the conductivity of nanocomposites increases with increasing SWNT loading for both PPEC8/SWNT and PPEOC8/SWNT composites. Remarkably, all PPE/SWNT nanocomposites exhibit very high electrical conductivity ($1-5 \times 10^3$ S/m for PPEC8/SWNT nanocomposites with 10–60 wt% SWNTs and $3-10 \times 10^3$ S/m for PPEOC8/SWNT nanocomposites with 10–60 wt% SWNTs), which is close to the in-plane conductivity (2×10^4 S/m)

of pure SWNT films [45]. The high conductivity is attributed to the high mass fraction SWNT (10–60 wt%) in the PPE/SWNT nanocomposites [17,44]. Our results are comparable to PS/SWNT nanocomposites with 80 wt% SWNTs (7000 S/m) [17] and PAN/SWNT nanocomposites with 40 wt% SWNTs $(1.5 \times 10^4 \text{ S/m})$ [46]. While percolation scaling laws of electrical conductivities of SWNT-based polymer nanocomposites are only strictly valid near the percolation threshold, percolation-like scaling at high volume fractions has also been reported [17]. According to the percolation theory, the conductivity (σ) of a percolative system is predicted to scale with volume fraction (V) as $\sigma = \sigma_0 \left(\frac{V - V_c}{1 - V_c}\right)^n \approx \sigma_0 V^n$, where σ_0 is the conductivity of the pure filler (in this case the conductivity of SWNTs), V_c is the percolation threshold, and *n* is the conductivity exponent. As the percolation threshold is very small in the SWNT-based polymer nanocomposites, it might be expected the approximation $\sigma \approx \sigma_0 V^n$ to hold in high volume fraction nanocomposites. In this work, we approximated mass fraction (M) as equivalent to volume fraction (V) and obtained $\sigma \approx \sigma_0 M^n$. This equation was fitted to the conductivity versus SWNT mass fraction data in Figure 9. The power law fitting gives a value of $\sigma_0 \sim 10^4$ S/m, which is in good agreement with the in-plane conductivity $(2 \times 10^4 \text{ S/m})$ of pure SWNT films [45]. The power law exponent n = 0.6-0.9 which is characteristic of hopping in conductive materials [47].



Figure 9. Data of electrical conductivities versus SWNT mass fraction for PPEC8/SWNT and PPEOC8/SWNT nanocomposites. The dashed lines are a power-law fit.

4. Conclusions

We have reported the dispersions and films of chromatic nanocomposites of poly(*p*phenylene ethynylene)s (PPEs) and single-walled carbon nanotubes (SWNTs). While the PPEs act as a dispersing agent to solubilize pristine SWNTs in organic solvents, SWNTs serve as a doping agent to enhance the stabilization of the excited states of chromatic PPEs. By adding SWNTs, the PPE solution color changes from yellow to blue for the dialkyl-PPE and from orange to green for the dialkyloxy-PPE. Optical properties of PPE/SWNT nanocomposites support chromatism and π - π interactions between PPEs and SWNTs.

By membrane filtration, chromatic films of PPE/SWNT nanocomposites are obtained with high mass SWNT loading. The tensile strength and modulus of resulting nanocomposite films increase more or less linearly with SWNT loading for both dialkyl-PPE and dialkyloxy-PPE. The effective stress transfer from PPEs to individual SWNTs contributes to the enhanced mechanical performance. High electrical conductivities of high mass fraction PPE/SWNT nanocomposite films are close to those of the neat SWNT films and conductivities versus SWNT mass fraction data display percolation-like scaling. Our work may provide a facile way to prepare highly conductive polymer nanocomposites for emerging applications.

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References

- 1. Negri, V.; Pacheco-Torres, J.; Calle, D.; López-Larrubia, P. Carbon nanotubes in biomedicine. *Top. Curr. Chem.* 2020, 378, 15. [CrossRef] [PubMed]
- 2. Vetrivel, R.; Navinselvak, C.; Samuel Ratna Kumar, P.S. Carbon nanotubes and its applications—A review. *Int. J. Mech. Prod. Eng. Res. Dev.* 2011, 2, 1099–1107.
- 3. Pan, H.; Li, J.; Feng, Y.P. Carbon nanotubes for supercapacitor. Nanoscale Res. Lett. 2010, 5, 654–668. [CrossRef]
- 4. Camilli, L.; Passacantando, M. Advances on sensors based on carbon nanotubes. Chemosensors 2018, 6, 62. [CrossRef]
- 5. Zhang, S.; Kumar, S. Carbon nanotubes as liquid crystals. *Small* 2008, *4*, 1270–1283. [CrossRef]
- 6. Zhang, S.; Kinloch, I.A.; Windle, A.H. Mesogenicity drives fractionation in lyotropic aqueous suspensions of multiwall car-bon nanotubes. *Nano Lett.* **2006**, *6*, 568–572. [CrossRef]
- Dyke, C.A.; Tour, J. Covalent functionalization of single-walled carbon nanotubes for materials applications. *J. Phys. Chem. A* 2004, 108, 11151–11159. [CrossRef]
- 8. Figueiredo, D.T.; Correia, A.A.S.; Hunkeler, D.; Rasteiro, M.G.B. Surfactants for dispersion of carbon nanotubes applied in soil stabilization. *Colloids Surf. A Physicochem. Eng. Asp.* **2015**, *480*, 405–412. [CrossRef]
- 9. Samanta, S.K.; Fritsch, M.; Scherf, U.; Gomulya, W.; Bisri, S.Z.; Loi, M.A. Conjugated polymer-assisted dispersion of single-wall carbon nanotubes: The power of polymer wrapping. *Accounts Chem. Res.* **2014**, *47*, 2446–2456. [CrossRef] [PubMed]
- Qiu, Z.; Hammer, B.A.; Müllen, K. Conjugated polymers-problems and promises. *Prog. Polym. Sci.* 2020, 100, 101179. [CrossRef]
 Zhang, Z.; Liao, M.; Lou, H.; Hu, Y.; Sun, X.; Peng, H. Conjugated polymers for flexible energy harvesting and storage. *Adv. Mater.* 2018, 30, e1704261. [CrossRef]
- 12. Inal, S.; Rivnay, J.; Suiu, A.-O.; Malliaras, G.G.; McCulloch, I. Conjugated polymers in bioelectronics. *Accounts Chem. Res.* 2018, 51, 1368–1376. [CrossRef] [PubMed]
- Lee, H.W.; You, W.; Barman, S.; Hellstrom, S.; Lemieux, M.C.; Oh, J.H.; Liu, S.; Fujiwara, T.; Wang, W.M.; Chen, B.; et al. Lyotropic liquid-crystalline solutions of high-concentration dispersions of single-walled carbon nanotubes with conjugated polymers. *Small* 2009, *5*, 1019–1024. [CrossRef]
- 14. Chen, Y.; Xu, Y.; Wang, Q.; Gunasinghe, R.N.; Wang, X.-Q.; Pang, Y. Highly selective dispersion of carbon nanotubes by using poly(phenyleneethynylene)-guided supermolecular assembly. *Small* **2013**, *9*, 870–875. [CrossRef] [PubMed]
- 15. Narizzano, R.; Nicolini, C. Mechanism of conjugated polymer organization on SWNT surfaces. *Macromol. Rapid Commun.* 2005, 26, 381–385. [CrossRef]
- 16. Matos, M.; Pinho, S.; Tagarielli, V. Predictions of the electrical conductivity of composites of polymers and carbon nanotubes by an artificial neural network. *Scr. Mater.* **2019**, *166*, 117–121. [CrossRef]
- 17. Blighe, F.M.; Hernandez, Y.R.; Blau, W.J.; Coleman, J.N. Observation of percolation-like scaling-far from the percolation thresholdin high volume fraction, high conductivity polymer-nanotube composite films. *Adv. Mater.* **2007**, *19*, 4443–4447. [CrossRef]
- Rosario-Canales, M.R.; Deria, P.; Kang, Y.; Therien, M.; Santiago-Aviles, J. Evaluation of composite electronic materials based upon single-wall carbon nanotubes and highly charged poly(aryleneethynylene)s for supercapacitor applications. *ECS Trans.* 2009, 16, 93–101. [CrossRef]
- Alturaif, H.A.; Alothman, Z.A.; Shapter, J.G.; Wabaidur, S.M. Use of carbon nanotubes (CNTs) with polymers in solar cells. *Molecules* 2014, 19, 17329–17344. [CrossRef]
- Landi, B.J.; Raffaelle, R.P.; Castro, S.L.; Bailey, S.G. Single-wall carbon nanotube-polymer solar cells. *Prog. Photovolt. Res. Appl.* 2005, 13, 165–172. [CrossRef]
- Lee, S.-H.; Ko, S.-J.; Eom, S.H.; Kim, H.; Kim, D.W.; Lee, C.; Yoon, S.C. Composite interlayer consisting of alcohol-soluble polyfluorene and carbon nanotubes for efficient polymer solar cells. ACS Appl. Mater. Interfaces 2020, 12, 14244–14253. [CrossRef] [PubMed]

- Schießl, S.P.; Fröhlich, N.; Held, M.; Gannott, F.; Schweiger, M.; Forster, M.; Scherf, U.; Zaumseil, J. Polymer-sorted semiconducting carbon nanotube networks for high-performance ambipolar field-effect transistors. ACS Appl. Mater. Interfaces 2014, 7, 682–689. [CrossRef]
- Chua, C.; Yeoh, K.H.; Woon, K. Hybrid carbon nanotube/polymer heterointerface organic field effect transistor. *Thin Solid Films* 2014, 556, 495–498. [CrossRef]
- 24. Park, S.J.; Lee, J.; Seo, S.E.; Kim, K.H.; Park, C.S.; Lee, S.H.; Ban, H.S.; Lee, B.D.; Song, H.S.; Kim, J.; et al. High-performance conducting polymer nanotube-based liquid-ion gated field-effect transistor aptasensor for dopamine exocytosis. *Sci. Rep.* 2020, *10*, 1–12. [CrossRef] [PubMed]
- 25. Bunz, U.H.F. Poly(aryleneethynylene)s. Macromol. Rapid Commun. 2009, 30, 772-805. [CrossRef]
- Bunz, U.H.F.; Seehafer, K.; Bender, M.; Porz, M. Poly(aryleneethynylene)s (PAE) as paradigmatic sensor cores. *Chem. Soc. Rev.* 2014, 44, 4322–4336. [CrossRef]
- 27. Ortiz, M.; Yu, C.; Jin, Y.; Zhang, W. Poly(aryleneethynylene)s: Properties, applications and synthesis through alkyne metathesis. *Top. Curr. Chem.* **2017**, 375, 69. [CrossRef]
- Lebouch, N.; Garreau, S.; Louarn, G.; Belletête, M.; Durocher, G.; Leclerc, M. Structural study of the thermochromic transition in poly(2,5-dialkyl-p-phenyleneethynylene)s. *Macromolecules* 2005, *38*, 9631–9637. [CrossRef]
- 29. Bunz, U.H.F. Poly(aryleneethynylene)s: Syntheses, properties, structures, and applications. *Chem. Rev.* **2000**, *100*, 1605–1644. [CrossRef]
- 30. Kang, W.Y.; Park, J.S. Supramolecular composite of single-walled carbon nanotubes with oligo(p-phenyleneethynylene)s-graft-poly(ethyleneoxide)s. *Fibers Polym.* **2012**, *13*, 1219–1224. [CrossRef]
- Ramos, J.C.; Flores, J.R.; Turlakov, G.; Moggio, I.; Arias, E.; Rodríguez, G. Self-assembly of a poly(phenyleneethynylene) on multiwall carbon nanotubes: Correlation of structural and optoelectronic properties towards solar cells application. *J. Mol. Struct.* 2020, 1222, 128845. [CrossRef]
- 32. Kang, Y.K.; Lee, O.-S.; Deria, P.; Kim, S.H.; Park, T.-H.; Bonnell, D.A.; Saven, J.G.; Therien, M.J. Helical wrapping of single-walled carbon nanotubes by water soluble poly(p-phenyleneethynylene). *Nano Lett.* **2009**, *9*, 1414–1418. [CrossRef]
- 33. Chen, J.; Liu, H.; Weimer, W.A.; Halls, M.D.; Waldeck, D.H.; Walker, G.C. Noncovalent engineering of carbon nanotube surfaces by rigid, functional conjugated polymers. *J. Am. Chem. Soc.* **2002**, *124*, 9034–9035. [CrossRef] [PubMed]
- 34. Jakubka, F.; Schießl, S.P.; Martin, S.; Englert, J.M.; Hauke, F.; Hirsch, A.; Zaumseil, J. Effect of polymer molecular weight and solution parameters on selective dispersion of single-walled carbon nanotubes. *ACS Macro Lett.* **2012**, *1*, 815–819. [CrossRef]
- 35. Chen, J.; Xue, C.; Ramasubramaniam, R.; Liu, H. A new method for the preparation of stable carbon nanotube organogels. *Carbon* **2006**, *44*, 2142–2146. [CrossRef]
- 36. Abdou, J.P.; Braggin, G.A.; Luo, Y.; Stevenson, A.R.; Chun, D.; Zhang, S. Graphene-induced oriented interfacial microstructures in single fiber polymer composites. *ACS Appl. Mater. Interfaces* **2015**, *7*, 13620–13626. [CrossRef]
- Abdou, J.P.; Reynolds, K.J.; Pfau, M.R.; van Staden, J.; Braggin, G.A.; Tajaddod, N.; Minus, M.; Reguero, V.; Vilatela, J.J.; Zhang, S. Interfacial crystallization of isotactic polypropylene surrounding macroscopic carbon nanotube and graphene fibers. *Polymer* 2016, *91*, 136–145. [CrossRef]
- 38. Zhang, S.; Zhu, L.; Wong, C.-P.; Kumar, S. Polymer-infiltrated aligned carbon nanotube fibers by in situ polymerization. *Macromol. Rapid Commun.* **2009**, *30*, 1936–1939. [CrossRef] [PubMed]
- Armas, J.A.; Reynolds, K.J.; Marsh, Z.M.; Fernández-Blázquez, J.P.; Ayala, D.; Cronin, A.D.; Del Aguila, J.; Fideldy, R.; Abdou, J.P.; Bilger, D.W.; et al. Supramolecular assembly of oriented spherulitic crystals of conjugated polymers surrounding carbon nanotube fibers. *Macromol. Rapid Commun.* 2019, 40, e1900098. [CrossRef] [PubMed]
- 40. Luo, Y.; Santos, F.A.; Wagner, T.W.; Tsoi, E.; Zhang, S. Dynamic interactions between poly(3-hexylthiophene) and single-walled carbon nanotubes in marginal solvent. *J. Phys. Chem. B* 2014, *118*, 6038–6046. [CrossRef] [PubMed]
- 41. Campbell, K.; Zappas, A.; Bunz, U.; Thio, Y.S.; Bucknall, D.G. Chemistry fluorescence quenching of a poly (para-phenylene ethynylenes) by C 60 fullerenes. *J. Photochem. Photobiol. A Chem.* **2012**, 249, 41–46. [CrossRef]
- 42. Adachi, N.; Okada, M.; Sugeno, M.; Norioka, T. Fluorescence turn-on chemical sensor based on water-soluble conjugated polymer/single-walled carbon nanotube composite. *J. Appl. Polym. Sci.* **2016**, *133*, 43301. [CrossRef]
- 43. Mao, J.; Liu, Q.; Lv, X.; Liu, Z.; Huang, Y.; Ma, Y.; Chen, Y.; Yin, S. A water-soluble hybrid material of single-walled carbon nanotubes with an amphiphilic poly(phenyleneethynylene): Preparation, characterization, and photovoltaic properties. *J. Nanosci. Nanotechnol.* **2007**, *7*, 2709–2718. [CrossRef] [PubMed]
- 44. Zhang, S.; Lin, W.; Wong, C.-P.; Bucknall, D.G.; Kumar, S. Nanocomposites of carbon nanotube fibers prepared by polymer crystallization. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1642–1647. [CrossRef] [PubMed]
- Sreekumar, T.V.; Liu, T.; Kumar, S.; Ericson, L.M.; Hauge, R.H.; Smalley, R.E. Single-wall carbon nanotube films. *Chem. Mater.* 2003, 15, 175–178. [CrossRef]
- 46. Guo, H.; Sreekumar, T.; Liu, T.; Minus, M.; Kumar, S. Structure and properties of polyacrylonitrile/single wall carbon nanotube composite films. *Polymer* **2005**, *46*, 3001–3005. [CrossRef]
- Kilbride, B.E.; Coleman, J.N.; Fraysse, J.; Fournet, P.; Cadek, M.; Drury, A.; Hutzler, S.; Roth, S.; Blau, W. Experimental observation of scaling laws for alternating current and direct current conductivity in polymer-carbon nanotube composite thin films. *J. Appl. Phys.* 2002, 92, 4024–4030. [CrossRef]