# Tailoring Triblock Copolymers for Dispersion of Individual, Pristine, Single-Walled Carbon Nanotubes in Organic Solvents

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Triblock copolymers, polyethylene oxide-(hexa-*p*-phenylene)-polyethylene oxide, were synthesized and used for dispersing single-walled carbon nanotubes (SWNT) in organic solvents. The resulting dispersions comprise mostly of individual tubes, as indicated by transmission electron microscopy at cryogenic temperatures. The dispersions could be dried and redispersed by the addition of a solvent, offering a useful method of application of predispersed SWNT. In situ optical spectroscopy indicates that the block copolymers which self-assemble in the native solution physically adsorb to the SWNT surface via the hexa-*p*-phenylene moiety. The noncovalent, weak adsorption competes with the polymer self-assembly, as clearly indicated by the emission spectra. The balance between self-assembly and adsorption is sensitive to the length of ethylene oxide side chains. The approach presented here may serve for optimization of the structure and composition of polymeric dispersants where one can chose between a long tail and a long adsorbing moiety, according to the specific needs presented by different applications of SWNT.

## 1. Introduction

Single-walled carbon nanotubes (SWNTs) are graphitic structures with a typical diameter of 0.8−2 nm and a length of up to millimeters.[1] The unique structural, mechanical, and electronic properties of the individual tubes offer promise in diverse fields of application including molecular electronics, composite materials, energy storage, and biomedical applications.[2,3] A major obstacle for SWNT utilization is their low dispersibility resulting from the high cohesion energy among pristine tubes. With a typical contact energy of 40000 kT, for 1 $\mu$m long SWNT,[4−6] the tubes form crystalline bundles or ropes of about a hundred tubes that further entangle into networks and that are nondispersible in most common solvents. Yet, dispersion of SWNT in a solvent is a crucial step for most applications. Thus a variety of pathways were devised for exfoliation of SWNT bundles into individual tubes and the dispersion of the debundled tubes in aqueous and organic solvents.[7]

Among the more challenging applications are SWNT-conjugate polymers composites where SWNTs are expected to function as an active component in electronic and optoelectronic applications. To achieve this goal the dispersion route has to fulfill a severe set of requirements including dispersion of *individual* SWNT in the limited selection of organic solvents that dissolve conjugated polymers, and the dispersion mechanism should not impair the electronic structure of the pristine tubes. The latter requirement excludes the use of covalent functionalizetion[8] as the approach is *highly interventional*[6,9] and transforms sp$^2$ bonded carbons into sp$^3$ and results in localization of the $\pi$ electrons. Indeed quantitative Raman spectroscopy of acid-oxidized SWNT[10] reveals notable changes in the intensity of the D-band (frequency 1350 cm$^{-1}$) indicating significant structural modification of treated SWNT, disruption of the conjugated electronic structure, and modification of the conjugation length of the tubes and consequentially their transport properties.[10]

The *weakly interventional*[6] approach for dispersion of SWNT is essentially different from the *highly interventional* approach. Here, the structure and function of the pristine tubes are preserved while bundling and aggregation are prevented. The approach relies on the introduction of weak repulsion (on the order of a few $k_BT$) at a large intertube distance where the attractive interaction between adjacent tubes is much smaller than $k_BT$.[5,6,11]

A good candidate for a repulsive interaction that fulfills these requirements is the (steric) long-ranged repulsion among tails of physically adsorbed block copolymers[12−14] in good solvent conditions. As demonstrated in Figure 1 the procedure described previously[5,14] results in exfoliation of SWNT bundles and (physical) adsorption of block copolymers onto the tubes. The adsorbed block copolymers induce a long ranged, weak repulsion among the polymer-decorated tubes[14,15] that suffices to prevent aggregation, bundling, and agglomeration of CNT in liquid media.

Recent studies that focused on the utilization of block copolymers for dispersion of SWNT in selective solvents[16] highlighted the role of the (soluble) A block in the stabilization mechanism of dispersed individual SWNT. It was shown that poly(ethylene oxide), PEO, blocks are efficient repellants in a variety of solvents and environments,[17,18] where polymer tails

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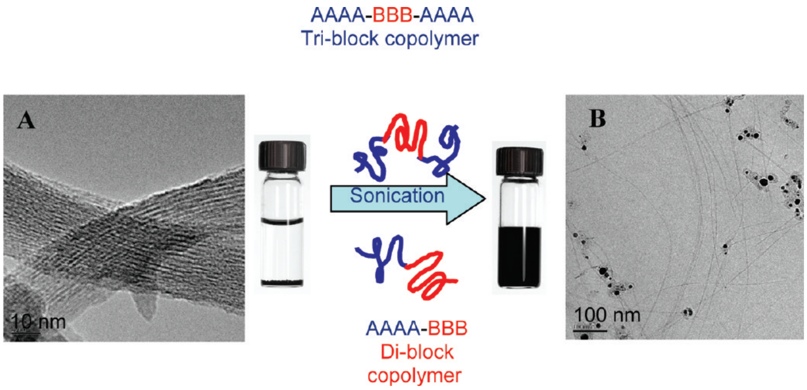


**Figure 1.** As-prepared SWNTs form bundles as observed in the high-resolution TEM image. A powder of as-prepared SWNT can not be dispersed in organic or aqueous liquids (A). Sonication in the presence of block copolymers leads to exfoliation of SWNTs, adsorption of the block copolymers (via the B block), and formation of black inklike dispersions of individual SWNT as indicated by cryo-TEM images of the dispersions (B).[5,6,14]

of short to medium chain length provide a high enough (~5 $k_BT$) steric barrier that prevents aggregation of dispersed tubes and lead to the formation of long-lived dispersions.[5,14]

An equally important role is played by the anchoring B block. Aiming at applications that rely on the electronic properties of the dispersed tubes the design of the B-block is even more challenging.[12] On the one hand, one aims to minimize the distortion of the conjugated $\pi$ -system of the SWNT utilizing relatively weak ($<k_BT$) adsorption per adsorbing segment; on the other hand, the overall tethering energy per chain should exceed $k_BT$ to ensure irreversible tethering of the dispersing agent to the surface. Here, one may take advantage of the versatile nature of polymeric moieties and search for the minimal number of monomers that provide sufficient anchoring energy for attaching the block copolymer to the tube surface. The tethering energy per monomer is then determined by the specific interactions between the B block and the SWNT at given solvent conditions and the overall tethering energy by the number of adsorbing segments.

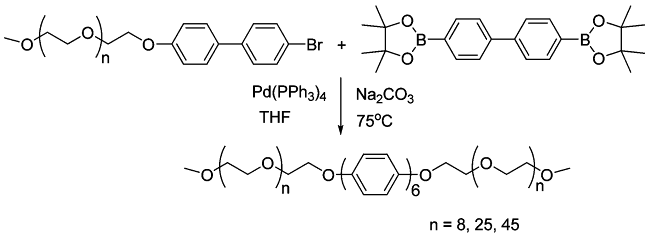
Aiming at dispersing SWNT in organic solvents that solvate electronically functional organic moieties, such as conjugated polymers, one is faced with a nontrivial challenge of designing a B block that would experience net attraction to the $\pi$-conjugated SWNT surface that is higher than the solvent− surface interaction. We can define the surface effective attraction between the adsorbing block and the nanotube as $\chi_{ps} = (U_{sol-sur} - U_{pol-sur})/k_BT$ where $U_{i-sur}$, $i =$ polymer or solvent, represents the attraction between species $i$ and the surface. A positive value of $\chi_{ps}$ is required for adsorption to occur.[10] As each of the $U$ terms measures the difference between the attraction of a given species to its own type of molecules and to the surface, the specific chemical nature of the adsorbing block and the solvent determines the strength of the polymer−surface interaction, $\chi_{ps}$. That in turn, together with the polymer chain length, determines the surface concentration of the adsorbed polymer and consequentially its dispersing power.[14] We note that when a block copolymer is used as a dispersing agent it is also important to prevent competitive adsorption of the soluble (A) block to the SWNT surface.

Here we present the design, synthesis, and characterization of a series of triblock copolymers $(PEO)_n(Ph)_6(PEO)_n$ that combine a conjugated moiety, the hexa-*p*-phenylene, and a good steric repellant (in the relevant solvents), PEO, of different chain lengths. The study focuses on organic solvents that are commonly used for dissolution of conjugated polymers for electronic and optoelectronic applications (toluene, chloroform, and 1,2-dichlorobenzene (dCB)).

**TABLE 1: Characteristics of the Pluronic PEO−PPO−PEO Copolymers**

| polymer | $M_w$ | PEO wt% | product no. |
|---|---|---|---|
| P103 | 4950 | 30% | 586460 |
| F127 | 12600 | 70% | 583106 |

**SCHEME 1: Synthesis of the $(PEO)_n$-$Ph_6$-$(PEO)_n$ Triblock Copolymers**



## 2. Experimental Section

**2.1. Materials and Methods.** ***Dispersing Agents.*** The following block copolymers and surfactants were purchased and used as received: poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide), $(PEO)_n(PPO)_m(PEO)_n$ (BASF)), P103, and F127 (Table 1, the Pluronic triblock copolymers were received as a gift from BASF AG Germany) $(PEO)_{2000}(PDMS)_{2000}$-$(PEO)_{2000}$ (Polymer Source Canada), and $(PEO)_{1900}(PB)_{1220}$ and $(PEO)_{1300}(PB)_{2500}$ (Polymer Laboratories, England).

***Carbonaceous Materials.*** (1) Raw SWNT synthesized by arc discharge were purchased from Carbolex Inc. USA (SWNT(AP)) and used as received. According to the specifications by the manufacturer, the as-prepared AP grade consists of 50−70 vol % SWNT, graphite cobalt, and nickel (ca. 20 nm in diameter). (2) MWNT produced by catalytic chemical vapor deposition were purchased from INP, Toulouse, France. The powder contains 95 vol % MWNT, tube diameter above 20 nm and length of micrometers, specific area 700−1000 $m^2/g$.

***Solvents.*** Analytical grade toluene, chloroform, dCB (Frutarom, Israel).

***Surfactants.*** Brij (78, 700 Sigma) $C_{18}H_{37}(OCH_2CH_2)_nOH$, n ≈ 20, 100.

**2.2. Synthesis of the Block Copolymers.** The block copolymers were synthesized by standard Suzuki cross coupling methods by assembling methoxy-terminated polyethylene glycol (PEG) derivatives of bromobiphenyl and biphenylboronic esters (Scheme 1).[20] Thus, three triblock copolymers with different PEG lengths ($n = 8$, 24, and 44) were prepared while the length of the oligophenylene was kept constant.

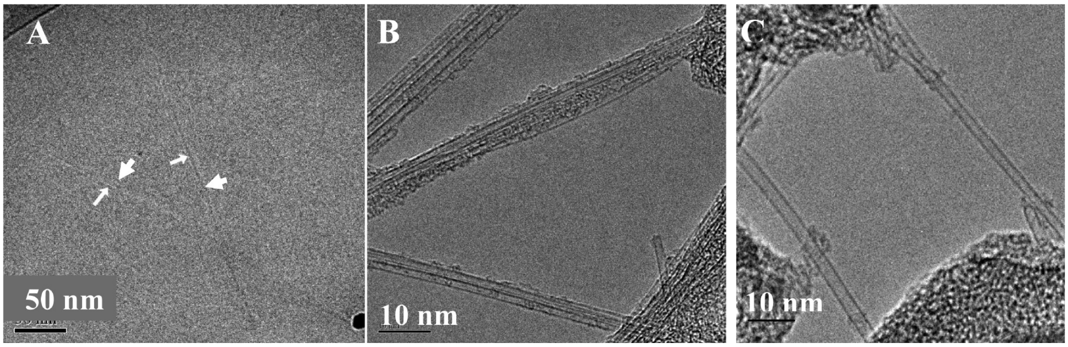


**Figure 2.** Electron microscopy images of stable dispersions. (A) Cryo-TEM image of SWNT in toluene dispersion of 2 wt % $(PEO)_{25}(Ph)_6(PEO)_{25}$. The arrows point to individual SWNT. Note that the contrast between carbon-based SWNT and the vitrified organic matrix is much lower than that between carbon-based SWNT and vitrified aqueous systems, which in itself is rather limited. In addition, nonaqueous specimens are highly sensitive to the electron beam. HRTEM images of dried specimens prepared from dispersions of SWNT (B) in chloroform using $(PEO)_{45}(Ph)_6(PEO)_{45}$ (2 wt %) and (C) in dCB using $(PEO)_8O(Ph)_6$ $(PEO)_8$ (1 wt %) (for cryo-TEM images in dCB see Figures S7 and S8 of the Supporting Information).

The polymers were purified by silica gel chromatography to remove starting materials (unreacted PEG-diphenyl bromide) and traces of catalyst. All compounds were pure as determined by $^1$H and $^{13}$C NMR, and their structure was confirmed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS, see Supporting Information).

**2.3. Preparation of Dispersions.** Liquid dispersions were prepared by dissolving a block copolymer (or a surfactant) in the solvent to form solutions of desired concentrations. The solutions were mixed for about 2−3 days using a magnetic stirrer or a roller. A powder of as-prepared nanotubes was sonicated mildly (50 W, 43 kHz) for 1 h in the polymeric solution (these conditions were shown not to damage the tubes or the polymers).[5,11] Following the sonication the dispersions were centrifuged (at $\sim 3 \times 10^4$ g for 20 min) and the supernatant (the dispersion) was decanted from above the precipitate. The dispersions were characterized using thermal gravimetric analysis (TGA) and Raman spectroscopy (see Supporting Information).

**2.4. TEM.** Direct imaging of the dispersed SWNT was carried following thermal quenching (toluene, dCB) for cryo-TEM, or drying for HRTEM.

While most of the cryo-TEM work reported to date involves water-rich systems, few examples of cryo-TEM of nonaqueous systems were reported.[21,22] Sample preparation for cryo-TEM measurements was carried out by deposition of a drop of the dispersion on a TEM grid (300 mesh Cu grid) coated with a holey carbon film (Lacey substrate-Ted Pella Ltd.). The difficulty of forming thin liquid films on the grid due to the fast evaporation of the solvent and the need to avoid the usage of ethane, which is the preferred cryogen but dissolves toluene and dCB, complicates sample preparation. In this study the vitrification of organic solvent-based samples was done by directly plunging the specimen into liquid nitrogen.[11] Although liquid nitrogen is not a good coolant because of its narrow liquid temperature range, it was still possible to produce vitrified samples. The samples were examined at −178 °C using a FEI Tecnai 12 G$^2$ TWIN TEM equipped with a Gatan 626 cold stage, and the images were recorded (Gatan model 794 CCD camera) at 120 kV in low-dose mode. Samples for HRTEM imaging were prepared by placing a droplet of the dispersion on a TEM grid (300 mesh Cu, Ted Pella) and allowing the solvent to evaporate.

**2.5. Spectroscopic Characterization: UV−Vis Absorption.** A Varian Cary Eclipse spectrofluorometer was used to measure the photoluminescence (PL) spectra of block copolymer and SWNT dispersions excited at 380 nm.

## 3. Results

Triblock copolymers $(PEO)_n(Ph)_6(PEO)_n$ were used for dispersing SWNT in toluene, chloroform, and dCB following the procedure described above. Apparently stable dispersions were centrifuged (at 4500 rpm for 20 min) and designated as "stable" if aggregation and phase separation were not observed following centrifugation. In a typical experiment polymer solutions (0.5 to 5 wt %) of the dispersing agent were prepared, the dry powder of CNT was added (0.1 wt %) sonicated and visually examined. As demonstrated in Figure 1, visual inspection enables one to discriminate between nondispersed (Figure 1A) and dispersed samples (Figure 1B). The microscopic structure of the dispersions was examined using cryo-TEM (toluene solutions, Figure 2A, dCB, Supporting Information) and HRTEM (Figure 2B).

Cryo-TEM and HRTEM images suggest that the dispersions are composed of individual SWNT, small bundles, and catalyst particles. The length of the observed SWNT is well above 1 $\mu$m.

Chloroform and toluene dispersions were found to be stable for days at room temperature (25 °C), while dispersions in dCB were stable for weeks following longer periods of incubation partial aggregation took place. Chloroform dispersions sonicated and stored at 4 °C were found to be stable for more than 4 months. Furthermore, we found that the dispersions could be dried and redispersed by shaking the dried powder in the solvent or by applying a short sonication at mild conditions (as above). This behavior is characteristic of sterically stabilized dispersions.[23] The redispersed powder resulted in the formation of black inklike dispersions as presented in Figure 3A. The microscopic structure of the dispersions formed by redispersion was examined using HRTEM. As can be seen in parts B and C of Figure 3, the dispersion is mostly composed of individual tubes and small bundles.

To determine the efficiency of the different dispersing agents, we characterized the minimal polymer concentration (designated the threshold concentrations $C_T$) necessary for the formation of dispersions of individual SWNT in each of the solvents. In a series of experiments the concentration of SWNT was kept constant at 0.1 wt % while the polymer concentration was varied between 0.1 to 3 wt %. Typical $C_T$ values are in the range of 0.5 to 2 wt %, suggesting a weight ratio of SWNT:dispersing polymer ratio of 1:2.5 up to 1:10 (Table 2).

The data presented in Table 2 clearly indicates that the highest efficiency (SWNT: dispersing polymer ratio) is achieved using a short PEO moiety ($n = 8$) in dCB.

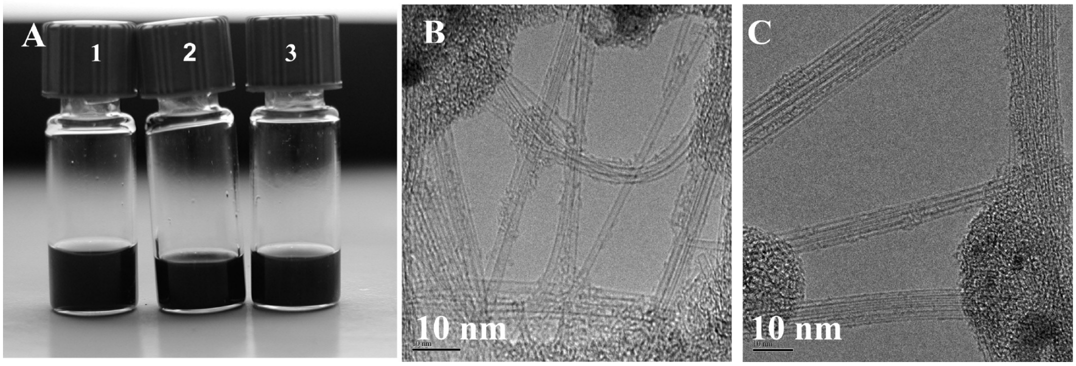


**Figure 3.** (A) An optical image of SWNT in (1) dCB solution of 1 wt % $(PEO)_8(Ph)_6(PEO)_8$, (2) 1.5 wt % chloroform solution of $(PEO)_{25}(Ph)_6(PEO)_{25}$, and (3) 2 wt % dCB solution of $(PEO)_{45}(Ph)_6O(PEO)_{45}$. HRTEM images of specimens prepared from dispersions that were dried from (2) and (3) and redispersed in dCB (B) without sonication (C) after mild sonication.

**TABLE 2: Threshold Concentration ($C_T$) Required for the Formation of a Stable Dispersion of SWNT in the Different Solvents**

| polymer | solvent | threshold concentration for dispersion $C_T$ (±0.05%) |
|---|---|---|
| $(PEO)_8(Ph)_6(PEO)_8$ | 1,2 dCB | 0.5% |
| $(PEO)_{45}(Ph)_6(PEO)_{45}$ | 1,2 dCB | 1.5% |
| $(PEO)_8(Ph)_6(PEO)_8$ | chloroform | 1% |
| $(PEO)_{25}$ $(Ph)_6(PEO)_{25}$ | chloroform | 1% |
| $(PEO)_{45}(Ph)_6(PEO)_{45}$ | chloroform | 2% |
| $(PEO)_{25}(Ph)_6(PEO)_{25}$ | toluene | 2% |

**TABLE 3: Surfactants and Block Copolymers**

| EO containing surfactants and block copolymers | no. EO units |
|---|---|
| Brij, $C_{18}H_{37}(OCH_2CH_2)_nOH$ | 20, 100 |
| $(PEO)_{1900}(PB)_{1220}$, $(PEO)_{1300}(PB)_{2500}$ | 43, 29 |
| $(PEO)_n(PPO)_m(PEO)_n$P103, F127 | 20, 106 |
| $(PEO)_{2000}(PDMS)_{2000}(PEO)_{2000}$ | 45 |

To test the role of specific interactions between the B-block and the dispersed moiety we performed two sets of control experiments. In the first set SWNT were replaced by MWNT. In the second set, a series of PEO-based block copolymers and surfactants was tested as the dispersing agent. The results are reported below.

We found that MWNT (0.1 wt %) could not be dispersed in the organic solvents using the series of the triblock copolymers $(PEO)_n(Ph)_6(PEO)_n$ up to 7 wt % of the block copolymers. Long sonication periods (of up to about 2 h) did not result in the formation of dispersions and the MWNT powder coagulated at the bottom of the vial.

Following the procedure described above, SWNT were sonicated in solutions of block copolymers with A blocks similar to those used above but different B block compositions, as listed in Table 3. The resulting dispersions were visually examined. We found that the block copolymers and surfactants listed in Table 3 did not disperse SWNT in the organic solvents tested.

**Optical Properties.** ***Solutions.*** The conjugation length of the hexa-*p*-phenylene endows it with strong absorption and emission in the visible region of the spectrum. Thus, the effect of homogeneous and nonhomogenous intermolecular interactions with neighboring molecules could be probed in situ.

The PL spectra of the native solutions of the triblock copolymers in dCB at $C_T$ (parts a−c of Figure 4) all show intense vibronic features centered at: 409, 430, 456, and 489 nm for the triblock with short $EO_n$ chains ($n = 8$) (Figure 4a): 396, 417, 441, 468 nm for the triblock with $n = 25$ (Figure 4b) and 395, 415, 440, 469 nm for the triblock with $n = 45$ (Figure 4c). Notably, the spectra blue shift and the vibronic features broaden as the PEO chain length increases. The PL spectrum of $(PEO)_8Ph_6(PEO)_8$ in dCB is in perfect agreement with the PL spectrum reported for a thin film prepared from the same material excited using the same wavelength (320 nm).[24] Moreover, the four intense vibronic features are also reported for thermally evaporated thin films of nonsubstituted hexa-*p*-phenylene.[25] Hence, we assign the well-resolved PL spectra of $(PEO)_8Ph_6(PEO)_8$ in dCB to *inter*molecular assemblies. The blue-shift and broadening of the vibronic features with PEO chain-length increase indicate a reduction in *inter*molecular interactions with increasing PEO chain length. The spectrum also shows an additional weak transition centered at ∼390 nm, probably originating from nonaggregated species in the solution.

The effect of PEO chain-length on the *inter*molecular assembly of the triblock copolymers in solution is further reflected in the PL spectra of the polymers in chloroform (parts d−f of Figure 4). Under the concentrations required for SWNT dispersion the triblock copolymer with short PEO chains, $n = 8$, assembles even in chloroform resulting in an intense vibronic PL spectrum (Figure 4d) similar to that of the same triblock polymer in dCB (parts a−c of Figure 4). Increasing PEO chain length to $n = 25$ reduces the resolution of the vibronic transitions and slightly blue-shifts the spectrum, with the transitions centered at 390, 407, 427, and 456 nm (Figure 4e). Furthermore, the PL spectrum of $(PEO)_{45}Ph_6(PEO)_{45}$ in chloroform at $C_T$ is broad and featureless with a peak centered at 407 nm and a weaker transition at 390 nm, as shown in Figure 4f. This spectrum is identical to that previously reported for dilute solutions of $PEO_nPh_6PEO_n$, $n = 3$, 8, 13, or 17, in chloroform, revealing that the long PEO chains dissociate the *inter*molecular assemblies in chloroform.[24,26]

The PL results in Figure 4 suggest that, in contrast with previous statements, the PEO block length does affect the optical properties of the triblock polymers.[24,26] This has been realized here for the first time due to the use of significantly longer PEO chains ($n = 45$) and solvents other than chloroform or water. This behavior is due to the interactions of the PEO and hexa-*p*-phenylene blocks with similar blocks of adjacent polymers, and with the solvents. Hexa-*p*-phenylene tends to form *inter*molecular assemblies derived by the $\pi-\pi$ interactions leading to extended conformations and vibronic PL features; in contrast, the high solubility and flexibility of the PEO chains imposes some torsion in the conjugated block leading to assembly dissociation and increased triblock polymer solubility.

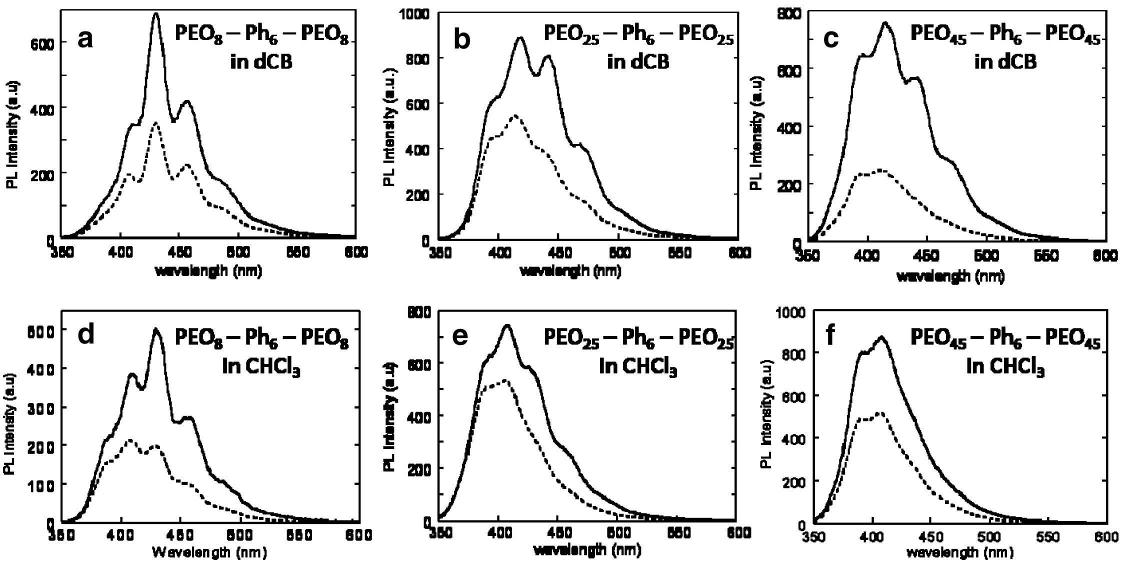


**Figure 4.** PL Spectra of Triblock Copolymer Native Solutions at Threshold Concentration for SWNT Dispersion $C_T$ (solid lines) and SWNT Dispersions (dashed lines) in dCB (a−c) or $CHCl_3$ (d−f).

***SWNT Dispersions.*** The optical properties were used to probe the molecular interactions between the triblock copolymers and the dispersed SWNT in dCB and chloroform. In general, the PL intensity of dispersion is lower than that of the corresponding native solution, probably due to scattering and absorption by the SWNTs. These processes are weakly wavelength-dependent as the electronic properties of the SWNT are extremely diverse. Notably, at the concentrations required for dispersion of SWNT (Table 2) assembly of the triblock copolymer is observed in the native dCB solutions (dashed lines in parts a−c of Figure 4) and in chloroform solutions of triblocks with short PEO moieties (dashed line in Figure 4d). In general, the PL spectra show that the homogeneous triblock interactions are reduced in the SWNT dispersions, evident from the decrease in vibronic features and slight blue shift of all spectra. The PL spectra of the SWNT dispersions in triblock copolymer with long PEO chain, $n = 45$, in dCB (Figure 4c), or the triblock copolymer with short PEO chain, $n = 8$, in chloroform (Figure 4d), is highly modified as compared to that of the respective native solutions. The resolved vibronic features in the PL spectra of $(PEO)_8Ph_6(PEO)_8$ in chloroform (Figure 4d) and $(PEO)_{45}Ph_6(PEO)_{45}$ in dCB (Figure 4c) are significantly broadened in the dispersions. In contrast, dispersion of SWNT has a minor effect on the PL spectra of triblock copolymer with short PEO chain in dCB (highly aggregated, Figure 4a), or triblock copolymer with long PEO chain, in chloroform (nonaggregated, Figure 4f). Therefore, the PL spectra indicate that the triblock copolymer disperse the SWNT through interactions of the conjugated hexa-*p*-phenylene block with the conjugated system of the SWNT. These interactions are at the expense of homogeneous triblock copolymer interactions leading to a reduction in the PL features of the triblock copolymer assemblies.

## 4. Discussion

Dispersion of SWNT in liquid media is a prerequisite for their utilization in a variety of applications.[27] Among the more efficient dispersing agents are triblock copolymers (A-B-A), shown before to disperse SWNT in aqueous and organic solvents.[5,6,14] The dispersion mechanism relies on adsorption of one of the blocks onto the nanotubes while the other blocks do not adsorb and dangle into the solution. In good solvent the dangling blocks form a steric barrier that prevents aggregation of polymer-decorated SWNT.[6,14] Previous studies focused on dispersions in selective solvent where the adsorbing block is under "poor solvent" conditions and the barrier forming block is that for which the block is in "good solvent" conditions. Yet some applications, such as those relevant for photoactive conjugated polymers, require the dispersion of SWNT in organic solvents that are good solvents for most of the B block candidates.[28,29] Under these conditions the adsorption of the B block relies on specific interactions between the dispersing polymer and the dispersed nanostructure. In this study we designed and utilized a series of triblocks based on a central conjugated block, hexa-*p*-phenylene, and two side blocks of PEO for dispersion of SWNT in toluene, chloroform and dCB. The hexa-*p*-phenylene B block used in this study was chosen under the assumption that a conjugated system would favorably and selectively interact with the conjugated system comprising the SWNT. Indeed dispersing agents based on this moiety were found to disperse SWNT but not MWNT, while nonconjugated B-blocks (Table 3) did not disperse the SWNT. The difference between the ability of block copolymers to disperse SWNT and MWNT is related to the surface density of the dispersing polymer and was discussed in detail by us in ref 14. The choice of the A blocks relied on previous studies, where detailed modeling of the steric barrier formed between SWNT decorated by dangling PEO tails[5,6] suggested that the strength and range of the steric repulsion induced by the polymers are monotonic increasing functions of both the chain length and polymer surface coverage. As was discussed before,[6] the very short range of the intertube attractive potential, originating from the nanometric diameter of SWNT and their hollow structure, renders relatively short PEO chains, in good solvent conditions effective stabilizers for SWNT.

A series of triblock copolymers with PEO block lengths of 8, 25, and 45 repeat units and an identical B block was synthesized and used for dispersion of SWNT. Black, inklike dispersions readily formed in toluene, chloroform, and dCB. Cryo-TEM imaging that reflects the solution behavior of dispersed SWNT at their native state,[30] carried out in toluene and dCB, indicated that the dispersions comprise of well dispersed individual SWNT and small bundles (Figure 2). The dispersions could be dried and redispersed by the addition of a solvent (without resonication), offering a useful method of application of predispersed SWNT.

The efficiency of the dispersing polymer as a function of the PEO block length and the solvent was investigated systematically. The data presented in Table 2 indicate that short PEO (8 repeat units) in dCB is the optimal dispersing agent as manifested by the lowest value of $C_T$. The molecular mechanism of the SWNT-triblock copolymer interactions were revealed via a detailed study of the optical properties of the dissolved block copolymers in the native solutions and in the dispersions. The optical behavior indicates that aggregation is preferred in dCB compared to chloroform and that short PEO chains and high concentrations induce *inter*molecular assembly, while low concentrations and long PEO chains lead to good dissolution of the polymer and dissociation of the assemblies. Dispersion of SWNTs in triblock copolymer solutions lead to a reduction in the PL features that characterize the triblock copolymer assemblies, indicating that nonhomogenous triblock copolymer−SWNT interactions replace homogeneous triblock copolymer interactions. We suggest that the correlation between aggregation of the short PEO triblock copolymer in dCB, evident from the PL spectra, is consistent with a higher value of $\chi_{ps,}$ and thus a higher adsorption onto the SWNT surface through interactions of the conjugated hexa-*p*-phenylene block with the conjugated system of the SWNT, leading to the superiority of this triblock copolymer as a dispersant for SWNT.

## 5. Summary and Conclusions

To conclude, we found that low-molecular weight block copolymers could be used for preparation of stable dispersions of individual SWNT in solutions of organic solvents.

The analysis presented above may serve for optimization of the structure and composition of block copolymers used for dispersion of SWNT in organic solvents, where one can chose between a long tail and a long adsorbing moiety, according to the needs presented by different applications of SWNT.

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**Supporting Information Available:** Synthetic procedures for the synthesis of the block copolymers and characterization ($^1$H and $^{13}$C NMR spectra, MALDI TOF MS) and cryo-TEM images of dispersed SWNT and TGA analysis. This material is available free of charge via the Internet at http://pubs.acs.org

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