

Research Article

Nucleation Mechanisms of Aromatic Polyesters, PET, PBT, and PEN, on Single-Wall Carbon Nanotubes: Early Nucleation Stages

Adriana Espinoza-Martínez,¹ Carlos Avila-Orta,¹ Víctor Cruz-Delgado,¹
Oscar Olvera-Neria,² Julio González-Torres,² and Francisco Medellín-Rodríguez³

¹Departamento de Materiales Avanzados, Centro de Investigación en Química Aplicada Boulevard,
Enrique Reyna 140 25294 Saltillo, COAH, Mexico

²Área de Física Atómica Molecular Aplicada (FAMA), CBI, Universidad Autónoma Metropolitana-Azcapotzalco,
Avenida San Pablo 180, Col. Reynosa Tamaulipas, 02200 México, DF, Mexico

³CIEP/FCQ, Universidad Autónoma de San Luis Potosí, Avenida Manuel Nava 6, 78210 San Luis Potosí, SLP, Mexico

Correspondence should be addressed to Carlos Avila-Orta, cavila@ciqa.mx

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Nucleation mechanisms of poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and poly(ethylene naphthalate) (PEN) on single-wall carbon nanotubes (SWNTs) are proposed, based on experimental evidence, theoretical epitaxy analysis, and semiempirical quantum chemical calculations. In order to elucidate early nucleation stages polyester-coated nanotubes were obtained from highly diluted solutions. High-resolution transmission electron microscopy (HRTEM) revealed helical morphologies for PET/SWNTs and PEN/SWNTs and the formation of lobules with different orientations for PBT/SWNTs. To explain the morphological behavior one model was proposed based on crystallographic interactions, that is, epitaxy. Theoretical epitaxy calculations indicated that epitaxy is not possible from the strict epitaxy point of view. Instead, aromatic self-assembly mechanism was proposed based on π - π interactions and the chirality of the nanotube. It was proposed that the mechanism implies two steps to produce helical or lobular morphologies with different orientations. In the first step polymer chains were approached, aligned parallel to the nanotube axis and adsorbed due to electrostatic interactions and the flexibility of the molecule. However, due to π - π interactions between the aromatic rings of the polymer and the nanotube, in the second step chains reoriented on the nanotube surface depending on the chirality of the nanotube. The mechanism was supported by semi-empirical calculations.

1. Introduction

During the last two decades carbon nanotubes (CNTs) were introduced in various semicrystalline polymers to enhance their mechanical and electrical properties, and to take advantage of outstanding properties and competitive benefits offered by carbon nanotubes [1, 2]. CNTs have played an important role not only in the reinforcement of semicrystalline polymer but also in their crystallization process [3, 4]. The CNTs main contributions observed in bulk crystallization of semicrystalline polymers include enhanced nucleation [5, 6], acceleration of crystallization [7, 8], reduced growth rate [9, 10], changes in spherulitic morphology [11, 12], and formation of imperfect crystallites [13, 14]. It has been reported that some semicrystalline polymers such

as polyolefins and polyamides can nucleate by means of different nucleation mechanisms in presence of nanotubes [12, 15, 16]. Epitaxial nucleation was found in polyamide 6 [12] and poly(vinyl alcohol) (PVA) [15] nanocomposites and was attributed to the structural similarity between the polymer and the substrate. Li et al. [16] proposed a size-dependent soft epitaxy (SSE) mechanism to explain the formation of nanohybrid shish kebab structures (NHSK), where matching constraint of classical epitaxy is relaxed. In the case of NHSK the shish is a carbon nanotube and the kebabs are formed by semicrystalline polymers such as polyethylene, nylon 66, polyvinylidene fluoride (PVDF), and poly(L-lysine) [16–18]. However, epitaxy and SSE mechanisms do not account for polymer chain features such as chemical structure, chain

conformation, helicity, aromatic ring or functional groups along the backbone and the electrostatic interactions with the surface of the nanotube. Recent reports revealed that the specific monomer structure such as aromatic rings and its spatial configuration affect polymer's affinities for nanotubes significantly. For example, Zheng et al. [19] reported in a molecular dynamics study that, for polystyrene (PS) and polyaniline (PANI), the interaction with carbon nanotubes is much stronger and increases more rapidly than that of polyethylene and polypropylene. Simulations done by Tallury and Pasquinelli [20] on a series of polymers showed that polymers with flexible backbones tend to wrap around the nanotube except for flexible backbone polymers with bulky and aromatic side groups such as PS and poly(methyl methacrylate) (PMMA).

Because carbon nanotubes have an aromatic structure, thus they can act as templates by means of π - π interactions for the nucleation of semicrystalline polymers containing aromatic rings in their backbone, such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and poly(ethylene naphthalate) (PEN). To test this hypothesis, the present work aims at investigating early nucleation stages of PET, PBT, and PEN in presence of nanotubes. Evidence of polyester-coated nanotubes is shown in HRTEM images, and theoretical epitaxy and semiempirical quantum chemical calculations are used to suggest suitable nucleation mechanisms.

2. Experimental Section

2.1. Materials and Methods. Three types of polyesters were used for coating carbon nanotubes, PET (Polyclear Splash, $M_w = 35,630$ g/gmol), PBT (190942, $M_w = 49,000$ g/gmol), and PEN (TEONEX TN8065S, $M_w = 42,921$ g/gmol) purchased from KOSA, Sigma-Aldrich, and Teijin Chemicals LTD, respectively. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) of purity >99.8 and chloroform of purity >99.8% (containing amylene (1-pentene) as stabilizer) were purchased from Sigma-Aldrich. Chloroform was dried for 5 hours over diphosphorus pentoxide and distilled under nitrogen. Single wall carbon nanotubes (SWNTs, P925 Elicarb) were kindly supplied by Thomas Swan with approximately diameter of 2 nm and <5% of metallic oxide.

SWNTs were coated with PET, PBT, and PEN by a simple solution mixing (Figure 1). Experimental conditions were chosen after a series of experiments where different polymer concentrations were tested to wrap the nanotubes with thin polymer layers (unpublished results). Polyesters were dissolved in HFIP and diluted with chloroform to reach a final concentration of 0.01 wt% in the chloroform/HFIP mixture (98:2 wt%). SWNTs (0.01 wt%) were dispersed in chloroform and ultrasonicated for 2 h in a Branson 2510 ultrasound bath. The polyester solutions were filtered through $0.45 \mu\text{m}$ filters to remove insoluble polymer and possible contaminant particles. The filtered polyester solution was then added to SWNT solution in a 1:1 (w/w) ratio. Finally, the polyester/SWNT solutions were ultrasonicated for 1 h and then allowed to stand for 24 h at 25°C . Samples

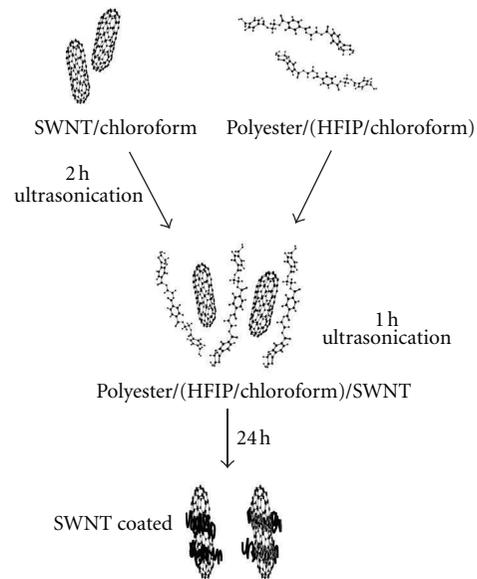


FIGURE 1: Experimental procedure for wrapping of SWNTs by using PET, PBT, and PEN polymers.

were collected placing a drop of solution on a Cu grid coated with amorphous carbon for further analysis. The solvent was evaporated at room temperature.

Morphology analyses of coated nanotubes were carried out in a transmission electron microscope (TEM) TITAN with an acceleration voltage of 300 kV. High resolution images (HRTEM) were obtained for specific areas.

3. Theoretical Calculations

3.1. Theoretical Epitaxy Nucleation Mechanism. To determine the possibility of epitaxy for PET, PBT, and PEN on SWNT, theoretical mismatch calculations were carried out. This mechanism is based on the structural similarity between the substrate and the overgrowth in the contact lattice planes. The degree of disregistry or mismatch is calculated as a percentage and defined by the following equation [21]:

$$\Delta = 100 * \frac{(d_{\text{overgrowth}} - d_{\text{substrate}})}{d_{\text{substrate}}}, \quad (1)$$

where d represents the distance between lattice planes or distance between molecules (or folded polymer chains) at the surfaces of the substrate and the overgrowth. A 10–15% disregistry is considered as the upper limit of epitaxial occurrence [21]. Further details related to theoretical epitaxial calculations will be discussed later.

3.2. Molecular Models of Polyesters. To study the interaction between the polyesters and nanotubes in the early nucleation stage, semiempirical quantum chemical calculations were performed with the MOPAC2009 [22] package using parametrized model 6 (PM6) [23]. Diethyl terephthalate

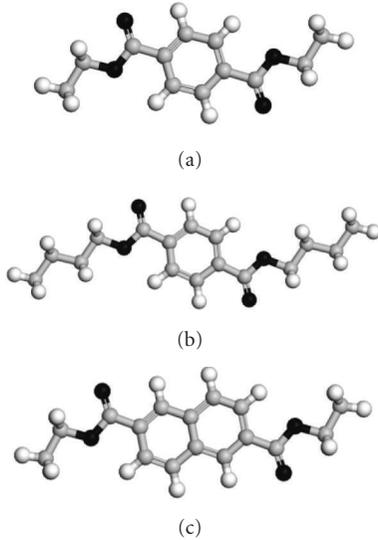


FIGURE 2: Chemical structures of representative PET, PBT, and PEN molecules: (a) diethyl terephthalate (DET), (b) dibutyl terephthalate (DBT), and (c) dimethyl 2,6-naphthalene dicarboxylate (DND). Dark, gray, and white spheres represent oxygen, carbon, and hydrogen atoms, respectively, and bonds are shown as the sticks connecting these atoms.

(DET), dibutyl terephthalate (DBT), and dimethyl 2,6-naphthalene dicarboxylate (DND) (Figure 2) were chosen as representative molecules of polymers PET, PBT, and PEN, respectively, for the model. In all the cases the phenyl or naphthalene ring and its two connected carbonyl groups are substantially planar as reported by other authors [24–26]. A systematic search of the global minimum on the potential energy curve was carried out using the gradient energy minimization with LowModeMD forcefield to find the most stable conformers of DET, DBT, and DND molecules. Subsequently, the geometries of all molecules were optimized separately using the semiempirical method PM6.

3.3. Molecular Models of Carbon Nanotubes. Armchair and zigzag nanotubes were chosen and their characteristics are shown in Table 1. For armchair nanotubes, the (4,4) and (5,5) SWNTs were studied, with a diameter of 5.42 y 6.78 Å, respectively, while for (8,0) and (10,0) SWNTs, the diameters were 6.26 and 7.38 Å, respectively. The length of SWNT was also varied to identify its effect on the adsorption energy.

Three possible interactions between polyester chains on the CNT surface were considered: face-to-face (F-F), perpendicular (PP), and transversal (T) (Figure 3). Each proposed interaction was built by using the optimized structures of polyester and carbon nanotubes and a full geometry optimization was performed to obtain the equilibrium nanotube-molecule structure with the PM6 method. Additionally, the interaction curve was determined by several static calculations, where the nanotube-molecule distance was maintained constant, while a partial geometry optimization was done. Adsorption energy (E_a) was calculated to determine the most energy-favorable configuration and

TABLE 1: Diameter and length of each nanotube used in semiempirical calculations.

| Type of nanotube | CNT diameter (Å) | CNT length (Å) | Identification |
|------------------|------------------|----------------|----------------|
| (4,4) SWNT | 5.42 | 17.22 | 447 |
| | | 19.68 | 448 |
| | | 22.14 | 449 |
| | | 24.60 | 4410 |
| (5,5) SWNT | 6.78 | 17.22 | 557 |
| | | 19.68 | 558 |
| | | 22.14 | 559 |
| | | 24.60 | 5510 |
| (8,0) SWNT | 6.26 | 17.04 | 804 |
| | | 21.30 | 805 |
| | | 17.04 | 1004 |
| (10,0) SWNT | 7.83 | 21.30 | 1005 |

defined as the total energy (E_{tot}) gained by molecule adsorption at equilibrium distance:

$$E_a = E_{\text{tot}}(\text{CNT} + \text{molecule}) - E_{\text{tot}}(\text{CNT}) - E_{\text{tot}}(\text{molecule}). \quad (2)$$

4. Results and Discussion

4.1. Morphology. Experiments were carried out to obtain morphological evidence of thin layers of polymer adsorbed on carbon nanotubes that contribute to support specific nucleation mechanisms during early nucleation stage. Figure 4 shows HRTEM images of the PET-, PBT-, and PEN-coated nanotubes. It is evident that in all three cases there is no periodically lamellae decoration as in the case of typical NHSK structures [16]. Instead, polymer chains seem to be forming helical wrapping as if following a path, being more evident for PET and PEN cases (Figures 4(a) and 4(c)). This helical wrapping on CNTs has been reported for biomacromolecules [27, 28] and poly(ethylene glycol) [29]. However, the origin of this morphology cannot be supported by the idea of helical chain conformation because it is well known that, unlike some biomacromolecules and PEG, the chains of PET, PBT, and PEN have a nearly planar zigzag conformation [26, 30, 31]. For the case of PBT, morphological evidence in Figure 4(b) shows the formation of a type of lobules with different orientations that probably serve as nuclei for the growth of crystals. These results suggest that specific mechanisms in early nucleation stage can be responsible for this effect.

4.2. Epitaxial Nucleation Mechanism. One of the potential mechanisms in the early nucleation stage that could explain the morphologies obtained is epitaxy, that is, crystallographic match. An isolated nanotube was considered for theoretical epitaxy calculations and the following three assumptions were made. First, for the case of carbon nanotubes the d_{001} graphene spacing is assumed to be the

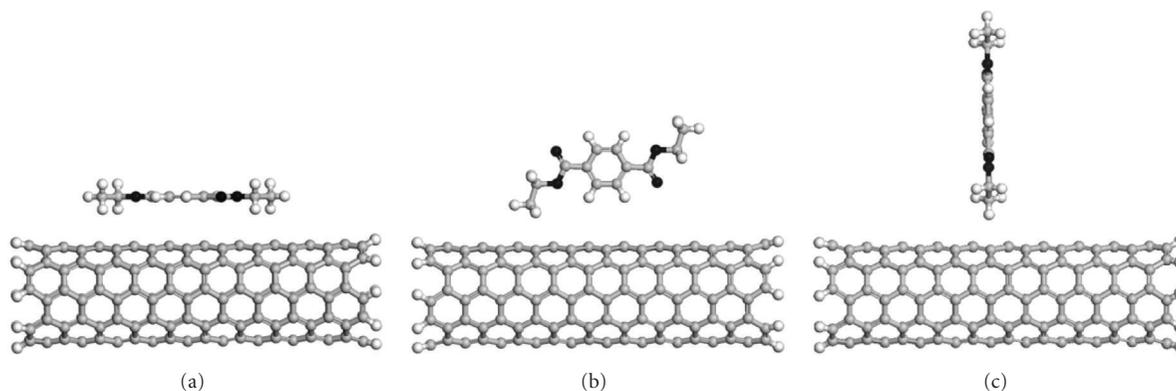


FIGURE 3: Possible configurations for the adsorption of DET, DBT, and DND molecules on SWNTs, (a) face-to-face (F.F), (b) transversal (T), and (c) perpendicular (PP) interactions.

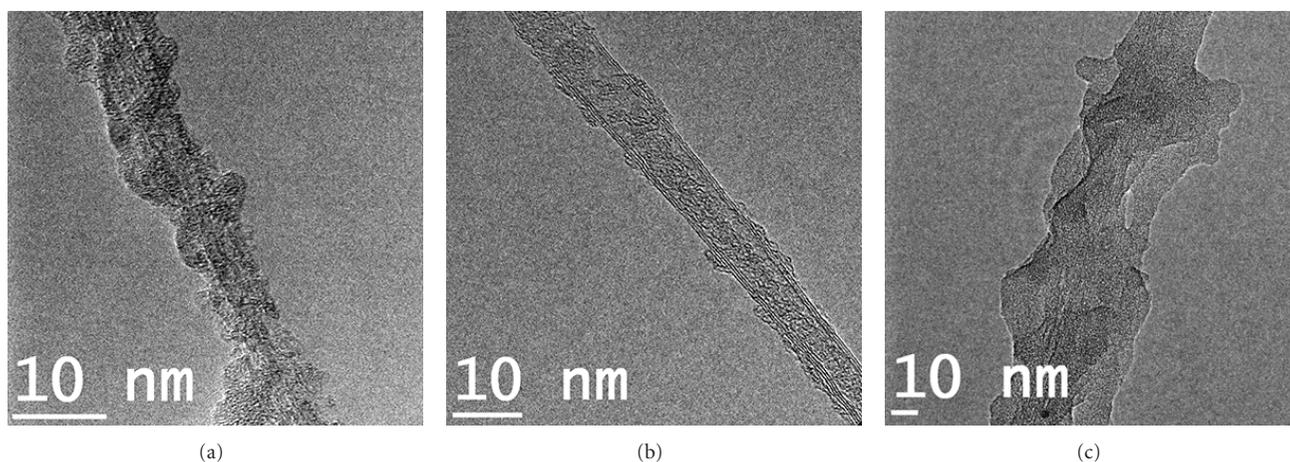


FIGURE 4: HRTEM images of poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and poly(ethylene naphthalate) (PEN) coated nanotubes.

TABLE 2: Epitaxial disregistry between carbon nanotubes and PET, PBT, and PEN.

| Polymer | d_{010}^1 (nm) | $d_{010 \text{ polymer}}/d_{100 \text{ graphene}}$, disregistry Δ (%) ² |
|---------|------------------|---|
| PET | 0.5178 [24] | 110.5 |
| PBT | 0.5124 [25] | 108.3 |
| PEN | 0.5710 [26] | 132.1 |

¹ Reported by other authors.

² Calculated.

contact plane surface and the curvature of the nanotube is neglected. Second, (100) planes of polyesters are considered parallel to the nanotube surface according to the results from the interaction of the polyesters with the nanotube obtained with the PM6 semiempirical approach (discussed later) and due to the geometric confinement. Third, the values of lattice spacing of polyesters to calculate the disregistry percentage were taken from the literature and shown in the second column of Table 2. For the cases of PBT and PEN, the values of lattice spacing correspond to the α form.

One important point to consider is that there are three possible chain directions that might develop upon such a surface due to the three-fold symmetry along the basal plane, each direction at 60° to any other direction, that is, depending on the chirality of the nanotube (see the example in Figure 5). This could explain not only the helical wrapping of PET and PEN, but also the multiple orientations of lobules in the case of PBT.

Attending the above considerations, disregistry for each system was calculated by means of (1) and the results are shown in Table 2. It observed that disregistries are higher than upper limits established for epitaxy. Therefore, epitaxy mechanism does not appear to be theoretically possible for the proposed model in the strict sense of epitaxy due to the lack of matching between crystallographic parameters of PET, PBT, and PEN, and those of nanotubes. Therefore, this nucleation mechanism based on crystallographic interactions cannot completely explain the obtained morphologies.

4.3. Other Nucleation Mechanisms. According to the results of mismatch, epitaxy for PET, PBT, and PEN on CNTs during early nucleation stage could not be theoretically

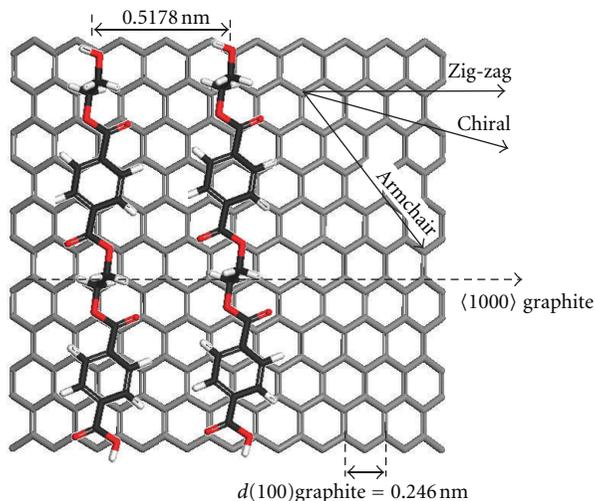


FIGURE 5: Schematic representation of (100) planes of PET parallel to graphene (002) basal plane.

supported. However, other nucleation mechanisms for early nucleation stage can be proposed if electrostatic interactions are taken into account. Because PET, PBT, and PEN contain aromatic units in their backbone, an aromatic self-assembly in the graphitic honeycomb of the CNTs can be possible by means of electrostatic interactions, where π - π interactions can be predominant. This phenomenon together with the chirality of the nanotube (as proposed for epitaxy) might define the orientation of polymer chains on the nanotube surface and the subsequent formation of crystals. Based on this assumption, it is suggested that in early nucleation stage there are two steps for the orientation of chains as shown in Figure 6. In the first step chains were approached, aligned parallel to the nanotube axis, and adsorbed due to electrostatic interactions. However, due to π - π interactions between the aromatic rings of the polymer and the graphitic honeycomb, in the second step polymer chains reoriented on the nanotube surface depending on the chirality of the nanotube. In this step, when the aromatic segments of polymer chains were adsorbed, the formation of nucleus started. The adsorption of polymer chains is influenced not only by the aromatic interactions but also by the flexibility of the polymer chain. In the case of PBT, it is well known that nuclei are formed faster than PET or PEN nucleus. Therefore, in early nucleation stage there is a competition between electrostatic interactions and the flexibility of the chains. It was reported by García-Gutiérrez et al. [32] and Mago et al. [33] that NHSK of PBT nanocomposites based on carbon nanostructures can be obtained by injection molding and precipitation processes. If the morphology obtained for PBT/SWCNT in our study is compared to that reported by other authors, it seems that, due to the fast nucleation rate of PBT, crystals growth is similar to that observed in polyethylene, that is, by forming lobules in early nucleation stage. Thus, there may be a competition between the flexibility of the chain and π - π interactions PBT on CNTs.

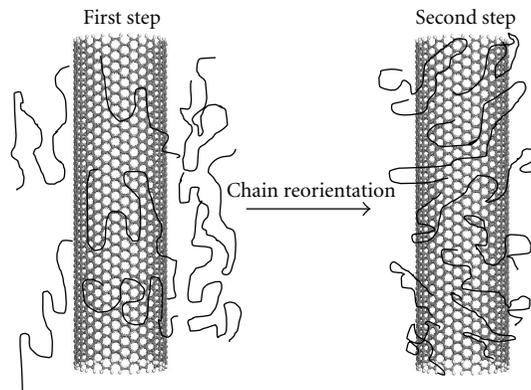


FIGURE 6: Schematization of the steps involved in the orientation of chains by means of aromatic self-assembly mechanism of PET, PBT, and PEN on CNTs.

It has also been reported for other authors that in the case of PET/CNTs [34] the attractive driving force behind the interfacial interaction might be possible π - π conjugation between polymer chains and nanotubes due to their common aromatic chemical units. However, it has not been supported. For this reason and to support the aromatic self-assembly mechanism proposed for PET, PBT, and PEN on carbon nanotubes, semiempirical calculations result in a useful tool.

As described above, three molecular configurations for the interaction of PET, PBT, and PEN with respect to the nanotube were studied (F, P, and T). It was found in the results of static semiempirical calculations that the equilibrium nanotube-molecule distance is between 3 and 4 Å for the three configurations. This distance is similar to that reported for other aromatic organic molecules interacting with CNTs [35]. Particularly, in the case of face-to-face configuration (Figure 7) the equilibrium distance is 3.5 Å, which agrees with the observation that crystals of many aromatic molecules form stacks with approximately parallel molecular planes separated by 3.3–3.6 Å [36]. This is also the case of concentric graphene layers distance in multiwall carbon nanotubes (MWNTs) and graphene layers in bulk graphite [37].

Figure 8 shows the interaction energy curves for three configurations of the DET, DBT, and DND molecules with different CNTs and, the diameter and length of armchair nanotubes are compared. It is observed that interaction energy in face-to-face configuration is higher than perpendicular or transversal configurations. The adsorption energy for face-to-face configuration is determined to be between -3.5 and -5 kcal/mol (see Table 3). For perpendicular and transversal configuration the adsorption energy is between -1 and -2 kcal/mol. These values of energy indicate that the interaction can be characterized as physisorption.

In the face-to-face configuration the adsorption energies are higher than the typical van der Waals interactions (<2 kcal/mol) and are between the strength hydrogen bonding and π - π interaction energy values (2–10 kcal/mol) [38]. Additionally, it is observed in Figure 8 that there is no

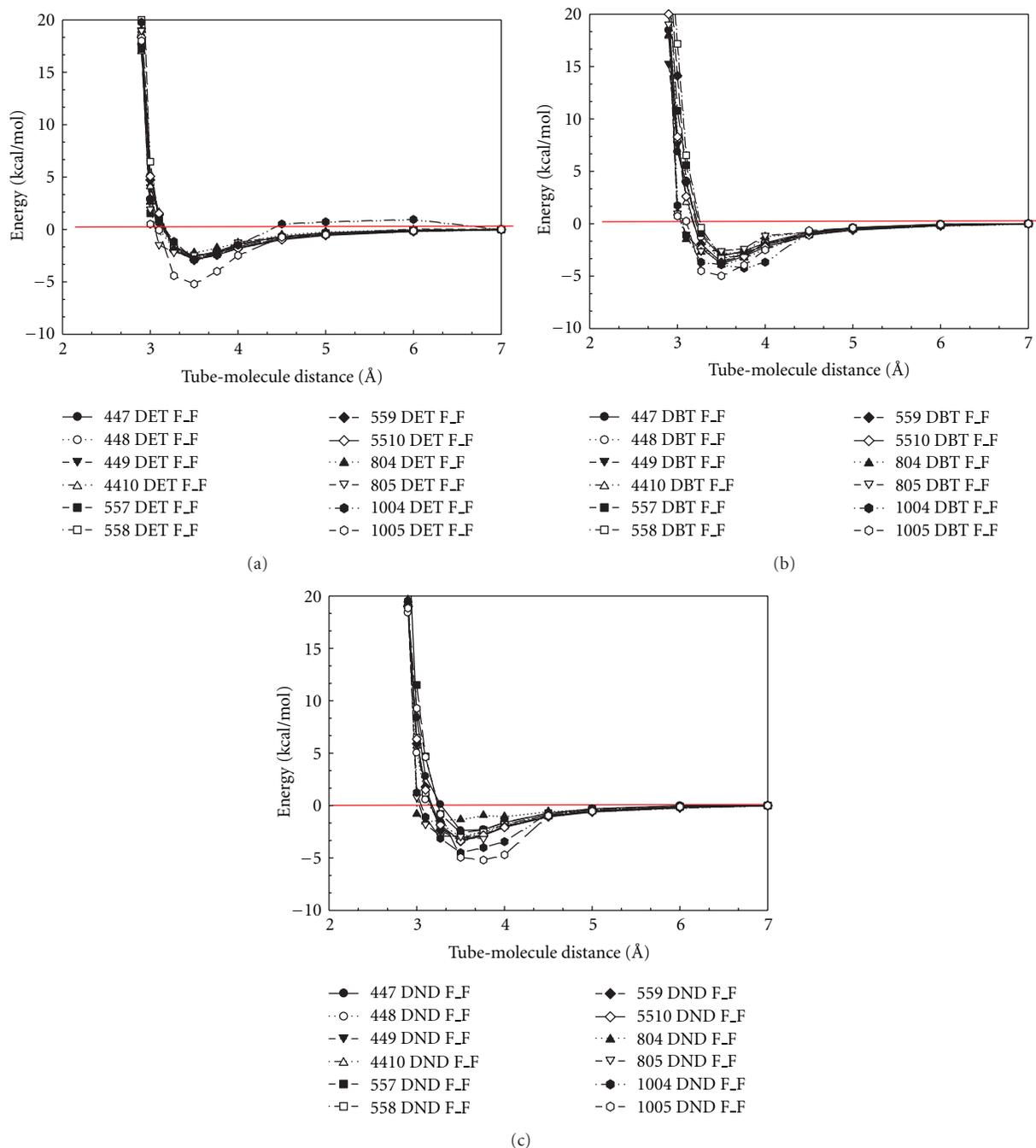


FIGURE 7: Interaction energy curves for face-to-face configuration of (a) DET, (b) DBT, and (c) DND with different SWNTs.

change in the interaction energy if (4,4) and (5,5) armchair nanotubes are compared and can be attributed to the small increase in the diameter of the tube (approx. 1.2 Å). With these results, it can be supported that aromatic self-assembly by means of π - π interactions (face-to-face) is the favorable configuration for the adsorption of aromatic polyesters PET, PBT, and PEN on SWNT in early nucleation stages.

Additional calculations for the face-to-face configuration of DET, DBT, and DND on nanotubes with different diameter and chirality were done to examine differences between

semiconducting zigzag and metallic armchair nanotubes (Table 3). It is noted that the differences in the adsorption energies between the armchair (4,4), (5,5) and the zigzag (8,0) nanotubes with similar diameter are very small, suggesting that the adsorption energy of DET, DBT, and DND on the CNT surface is independent of nanotube chirality. Similar results were found by Yu et al. [39] using the density functional theory (DFT) method for the adsorption of PVDF on CNTs. Interaction energy for the zigzag (10,0) nanotubes showed an increase of more than twice with respect to the

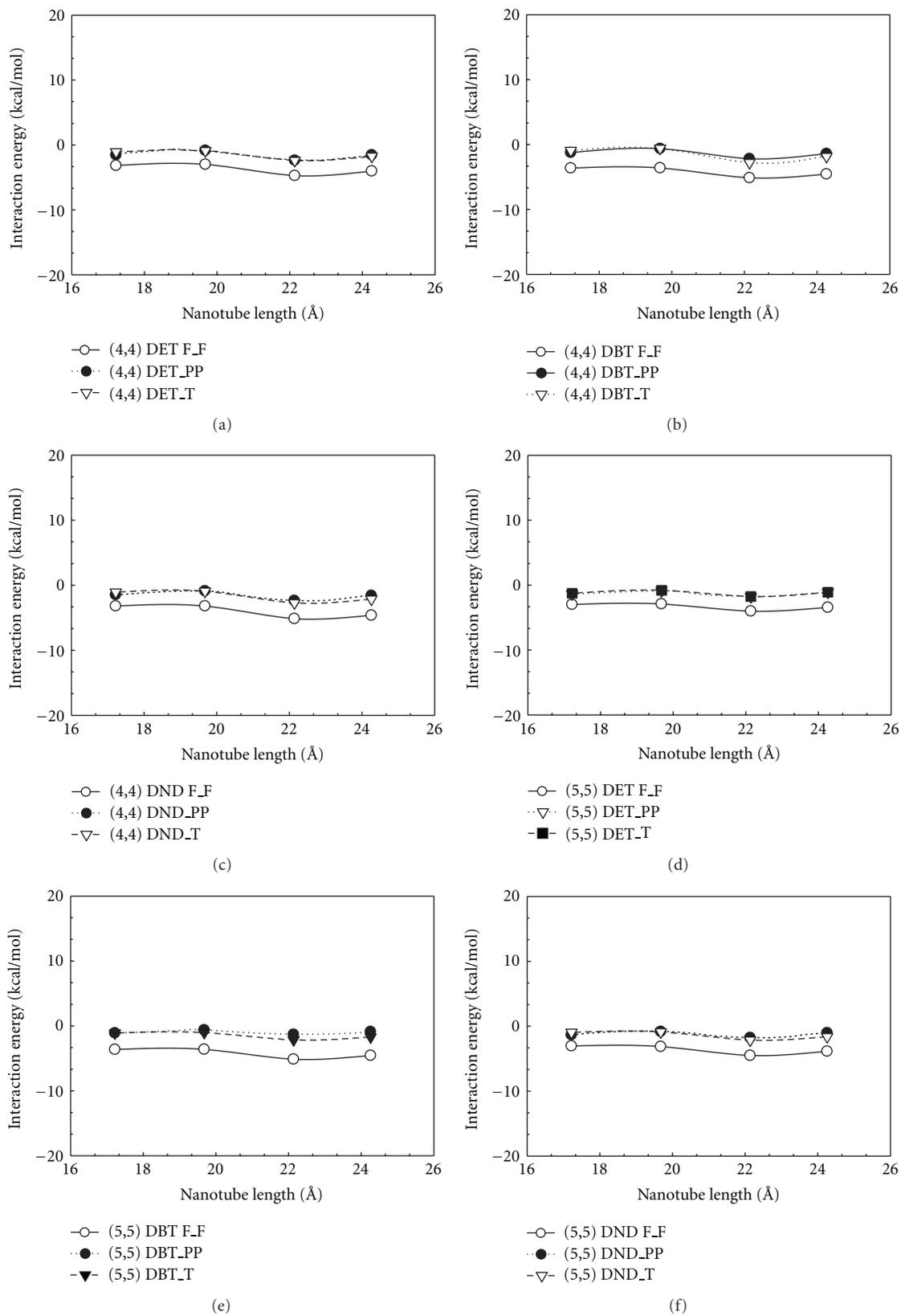


FIGURE 8: Intermolecular interaction between DET, DBT, and DND and (4,4) and (5,5) armchair nanotubes as a function of SWNT length in the face-to-face (F-F), transversal (T), and perpendicular (PP) configurations.

TABLE 3: Interaction energies for face-to-face configuration of DET, DBT, and DND on armchair and zigzag nanotubes.

| Nanotube | CNT diameter (Å) | CNT length (Å) | Interaction energy (kcal/mol) | | |
|--------------|------------------|----------------|-------------------------------|--------|--------|
| | | | DET | DBT | DND |
| 449 armchair | 5.42 | 22.14 | -4.73 | -5.80 | -5.15 |
| 559 armchair | 6.78 | 22.14 | -4.02 | -5.14 | -4.51 |
| 805 zigzag | 6.26 | 21.30 | -4.03 | -5.88 | -4.37 |
| 1005 zigzag | 7.83 | 21.30 | -16.49 | -12.45 | -19.31 |

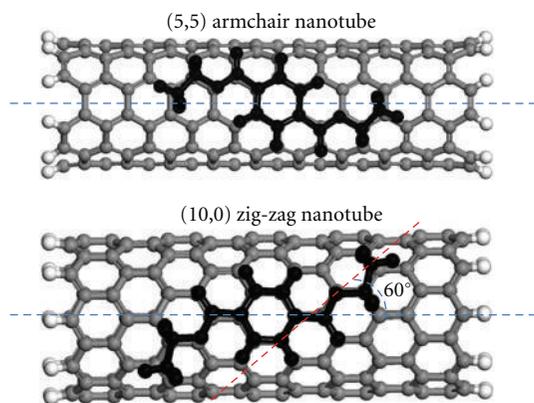


FIGURE 9: Orientations of DET on (5,5) armchair nanotube and (10,0) zigzag nanotube from semiempirical calculations.

other nanotubes (Table 3). It agrees with the results reported by Zheng et al. [19], that is, when the diameter of SWNT is increased, aromatic rings of the polymers can align parallel to the surface. Thus the π - π interactions between the aromatic rings and the SWNTs increase significantly. If this theoretical behavior is extrapolated to our experiments, that is, when the diameter of the nanotube is around 2 nm compared to the theoretical nanotubes with diameters between 5 and 8 Å, then molecules of aromatic polyesters PET, PBT, and PEN can interact in such a way with the surface of the nanotube that the aromatic self-assembly mechanism is feasible. In Figure 9 the orientations of DET molecules on (5,5) armchair nanotube and (10,0) zigzag nanotube from the semiempirical calculations are shown. It observed that in fact phenyl ring is assembled on the honeycomb of the nanotube, and polymer chain develops different directions depending on the chirality of the nanotube. For armchair nanotube the angle between the orientation of the aliphatic segments of polyesters and the tube axis tended to 0° and for zigzag nanotube 60°. This may support the reorientation of PET, PBT, and PEN chains in our two-step mechanism proposed for early nucleation stage.

The effect of the chemical structure of polyesters on the interaction energy with CNTs was also analyzed. It observed in the Table 3 that the higher interaction energy was for the zigzag (10,0) CNT with the DND molecule that represents PEN. Further, the interaction for the system DBT/SWNT is weaker than that presented with DET/SWNT. It indicates that the presence of two aromatic rings in the backbone, as

in PEN, promotes the adsorption on the nanotube surface through strong π - π interactions. Moreover, the aliphatic sections play an important role during the early nucleation stage because they help molecular diffusion and accelerate the nucleation process. Also, it was found that at equilibrium distance, the carbonyl group of DET/SWNT, DBT/SWNT, and DND/SWNT optimized structures remains in the plane of the aromatic ring for the systems molecule-nanotube (10,0) (in the face-to-face configuration). However, the dihedral angle of the aliphatic extremes decreases about 5° below the plane of aromatic ring. In summary, aromatic self-assembly was achieved in early nucleation stages of PET, PEN, and slightly for PBT on single wall carbon nanotubes.

5. Conclusions

Nucleation mechanisms of PET, PBT, and PEN in presence of carbon nanotubes were studied. Experimental evidence and theoretical calculations were used to elucidate and propose early nucleation stage mechanisms. Polyester-coated nanotubes were obtained from highly diluted solutions. The nanotubes were wrapped with thin layers of polymer and developed different morphologies. Helical morphologies for PET/SWNTs and PEN/SWNTs and lobules with different orientations for PBT/SWNTs were achieved. On the basis of epitaxial theoretical calculation for the proposed model, it revealed that epitaxy cannot explain the obtained morphologies in the strict sense of epitaxy due to the lack of matching between crystallographic parameters of polyesters and those of nanotubes. It was suggested that the aromatic units contained in the backbone of PET, PBT, and PEN led to an aromatic self-assembly mechanism in the graphitic honeycomb of the nanotubes by means of electrostatic interactions, where π - π interactions are predominant. It proposed that early nucleation stage implies two steps to produce helical or lobular morphologies with different orientations. In the first step polymer chains were approached, aligned parallel to the nanotube axis, and adsorbed due to electrostatic interactions and the flexibility of the molecule. However, due to π - π interactions between the aromatic rings of the polymer and the graphitic honeycomb, in the second step polymer chains reoriented on the nanotube surface depending on the chirality of the nanotube. The aromatic self-assembly mechanism was also supported by the results from semiempirical calculations where face-to-face configuration was the most stable for the adsorption of aromatic polyesters, and in the optimized systems chains oriented depending on the chirality of the nanotube. Also, energy calculations indicated that the presence of more aromatic rings in the backbone promotes the adsorption of polymer chains on the nanotube surface through π - π interactions. However, due to the larger aliphatic section of PBT and the lobular morphology on nanotubes it was clear that there is competition between electrostatic interactions and the chain flexibility during early nucleation stage.

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