Supporting Information for

Molecular Alignment of a Meta-Aramid on Carbon Nanotubes by In-Situ Interfacial Polymerization.

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S1. Molecular Dynamic Simulation

To conduct MD simulation of the ISIP reaction, the ReaxFF\textsuperscript{1} reactive force field must feature accurate parameters to representatively simulate the polymerization reaction and polymer-CNT interaction. ReaxFF force field parameters are the same as presented elsewhere\textsuperscript{2} for most species and that of Chlorine are taken from Wood. et al.\textsuperscript{3} Additionally, validation of the force field was conducted by comparing the polymerization energy barrier with that obtained by density functional theory (DFT) method. Specifically, the Becke, 3-parameter, Lee–Yang–Parr (B3LYP) approach with the 6-311G**++ basis set are used for DFT calculations. The optimized ReaxFF force field parameters result in a value of energy barrier of 13 kcal/mol, on-par with the 19 kcal/mol calculated by DFT calculations.

The MD simulation protocol for ISIP is divided in three stages described in Table S1. Structures are studied in the NVT ensemble at a temperature of 300K and using accelerated molecular dynamics. More details on accelerating the target reactions can be found elsewhere.\textsuperscript{2}
A time step of 0.25 fs is used, and the box dimensions are set at 80 x 80 x 81 Å³ in the case of circular CNTs, and a larger 130 x 70 x 51 Å³ in the case of flattened CNTs to accommodate the anisotropic shape of the nanotube.

Table S1. Molecular Dynamics (MD) simulation setup to study the influence of monomer concentration on PMPI-CNT interaction.

|                | Low monomer concentration simulation |          |          |          |
|----------------|--------------------------------------|----------|----------|----------|
|                | m-phenylene diamine (MPD)            | Isophthaloyl chloride (IPC) | Cyclohexanone |
| Stage 1        | 50                                   | 50       | 500      |
| Stage 2        | 50                                   | 50       | 250      |
| Stage 3        | 50                                   | 50       | 0        |

|                | High monomer concentration simulation |          |          |          |
|----------------|--------------------------------------|----------|----------|----------|
|                | m-phenylene diamine (MPD)            | Isophthaloyl chloride (IPC) | Cyclohexanone |
| Stage 1        | 250                                  | 250      | 500      |
| Stage 2        | 250                                  | 250      | 250      |
| Stage 3        | 250                                  | 250      | 0        |

In addition to studying ISIP in presence of circular CNTs (Figure 1), the ReaxFF reactive force field is also used to study the influenced of flattened CNTs (flCNTs) on molecular interaction with PMPI (Figure S1). To ensure comparable geometries between the circular and flattened CNT models, the dimensions of the flCNT-polyaramid simulation are assigned so that the distances from neighboring CNTs are almost identical for both cases in x and y directions. The depth of flCNT-polyaramid simulation box (z) is calculated so that the available space for monomers is identical for both cases of circular and flattened CNTs models. The same MD simulation protocol is also used on both cases (Figure S1a). While at low concentration (50 of each monomer), the Herman function relevant to the polymer backbone elements is similar for circular and flattened CNTs ($f \sim 0.8$) (Figure S1b), we notice that $f$ is greater for flattened CNTs than for circular CNTs when 250 of each monomer are initially introduced in the system (Figure S1c). Indeed, while $f \sim 0.4$ in the case of flattened CNTs, it varies between 0.2 and 0.3 when a circular CNT is studied. This can be explained by two main phenomena. First, flCNTs feature flat stable areas for which the polymer affinity and alignment are greater. The localization of macromolecular chains on thise
flat areas prevents the formation of polymer bridges between neighboring nanotubes by periodic boundary condition. Bridging results in overall loss of polymer alignment and occur when circular CNTs are studied (Figure 1e). Additionally, flattened CNTs feature a central area with no curvature, allowing for greater polymer alignment for short chains with lower backbone flexibility.

**Figure S1. MD simulation of ISIP in the case of flattened CNTs.** (a) Snapshot at subsequent stages of the simulations showing monomer molecules attaching to each other and building oligomers, as well as half the solvent molecules begin removed (Stage 2), and then all the solvent molecules being removed (Stage 3). The color scheme is that of Figure 3. (b) Herman function during stage 3 for a simulation featuring 50 and 250 of each monomer. Both simulations feature 500 cyclohexanone molecules. (c-d) Polymer morphology and spatial distribution of the normal vector to the PMPI aromatic rings at t=1500ps for an initial number of each monomer molecules of (c) 50 and (d) 250.

**S2. Materials and synthesis**

All chemicals were used as received and did not undergo any additional purification. Isophthaloyl Chloride (≥99%) was obtained from TCI America and stored under inert atmosphere to prevent hydrolysis of the compound. M-phenylene diamine (≥99%) was purchased from Millipore Sigma and was also stored under inert atmosphere. Cyclohexanone (ACS reagent, ≥99.0%), water (ACS reagent), and acetone (ACS reagent, ≥99.5%) were also obtained from Millipore Sigma. CNT
sheets were manufactured by Nanocomp Technologies, Inc using a floating catalyst chemical vapor deposition (CVD) process. After synthesis, the CNT sheets are liquid-saturated and stretched by ~35%, resulting in a final CNT Herman orientation function of 0.7. The sheets comprise of both circular and flattened CNTs, along with 5-10wt.% amorphous carbon and 10-20wt.% residual catalyst. Details on the ISIP synthesis can be found elsewhere.

S3. Characterization methods

Scanning Electron microscopy (SEM). SEM imaging was conducted on a Zeiss Gemini 450 SEM High-Resolution Scanning Electron Microscope (SEM) using the High-Resolution mode, the in-lens detector, an acceleration voltage of 3kV, and a probe current of 100 pA.

Fourier transform infrared (FT-IR) spectroscopy. FT-IR spectra were acquired with a Bruker ALPHA II FT-IR spectrometer equipped with the Platinum Attenuated Total Reflection (ATR) accessory. 128 scans were used for each acquisition and the raw signals were corrected by removing the baseline and removing atmospheric contributions using Bruker OPUS spectroscopy software. The average and standard deviation for relevant peak locations were obtained by measuring 5 composite samples synthesized at the same concentration.

Raman Spectroscopy. Raman Spectroscopy was conducted on a Renishaw Invia Reflex Raman Confocal Microscope, using a 532 nm laser (50 mW), a 1200 l/mm grating and a 100x objective. The Raman spectrum of pure PMPI was obtained with 5% laser power, 2 sec integration time and 15 accumulations. Neat CNT sheets and CNT-PMPI composites were cut and mounted on a 90° Specimen Mount (Ø32 x 12mm) to focus the laser spot on the cross-section of the composite. A CNT-PMPI composite sheet obtained using a monomer concentration of 0.150 mol.L\(^{-1}\) was chosen as it would feature a high polymer content (i.e. a more easily detectable polymer signal) while still exhibiting signs of strong CNT-polymer interaction through its FT-IR response. Numerous spectra were taken at different locations on the cross-section using the mapping functionality of Renishaw Windows®-based Raman Environment (WiRE) software. Acquisition parameters for both the neat and composite CNT sheets were 10% laser power, 30 sec integration time and 3 accumulations. Focus was maintained throughout mapping using Renishaw FocusTrack™ function. FocusTrack™ periodically checks and adjusts the sample focus between data acquisitions,
scanning over a pre-defined vertical range and finding the optimum focus (position of maximum laser intensity). For the CNT-PMPI composite, 2379 spectra were acquired over a 40 \times 20 \, \mu \text{m} area. For the neat CNT sheet, 100 spectra were acquired over a 10 \times 10 \, \mu \text{m} area. All spectra were cleaned by removing cosmic rays and subtracting baseline. Shape changes of the Raman spectra are analyzed by extracting partial Raman spectra (PRS) - also called component spectra - with a custom algorithm relying on Principal component analysis (PCA), and sparse non-negative matrix factorization (NMF). The sum of the PRS, i.e. the sum of its Raman-active structural species, describes the overall Raman spectrum of the characterized material.

**S4. Spectroscopy and peak assignment**

**Table S2.** Peak assignment for FTIR spectra as described in the literature,\textsuperscript{7,8} for neat PMPI synthesized by IP at a static liquid-liquid interface, and for PMPI-CNT composite obtained by ISIP.

| Neat PMPI synthesized by IP (cm\textsuperscript{-1}) | PMPI-CNT composites synthesized by ISIP (cm\textsuperscript{-1}) | Assignment of vibrational mode |
|-----------------------------------------------------|---------------------------------------------------------------|--------------------------------|
| 3305 (w)                                            |                                                               | N-H stretching vibrations in a secondary amide                  |
| 1646 (s)                                            | 1647 (s)                                                      | Amide I (C=O) stretching vibration                               |
| 1605 (s)                                            | 1603 (m)                                                      | Aromatic quadrant stretch (meta)                               |
| 1533 (s)                                            | 1528 (s)                                                      | Amide II vibration, \(\delta(\text{NH})\) and \(\nu(\text{CN})\) |
| 1484 (s)                                            | 1473-1480 (m)                                                | Aromatic semicircle stretch (meta)                             |
| 1432 (w)                                            | 1432 (w)                                                      | In-plane C-H bending                                            |
| 1409 (m)                                            | 1398-1406 (m)                                                | Aromatic in-plane C-H bend                                     |
| 1298 (w)                                            |                                                               | Aromatic C-N stretching                                        |
| 1242 (m)                                            | 1232 (m)                                                      | Amide III vibration, \(\nu(\text{CN})\), \(\delta(\text{NH})\), and \(\nu(\text{CC})\) |
| 1166 (w)                                            | 1160 (w)                                                      | CH deformation which are coupled to aromatic C-C stretch/C-H bend vibrations |
| 1080 (w)                                            |                                                               | Ring stretching-CH bending                                     |
| 933 (w)                                             |                                                               | CH deformation which are coupled to aromatic C-C               |
| PMPI (reported) (cm$^{-1}$) | Neat PMPI synthesized by IP (cm$^{-1}$) | PMPI-CNT composite synthesized by ISIP (cm$^{-1}$) | Assignment of vibrational mode |
|-----------------------------|------------------------------------------|-------------------------------------------------|-------------------------------|
| 1002 (vs)                   | 1001 (vs)                                |                                                 | Trigonal ring breathing vibration |
| 1180 (w)                    | 1193 (w)                                 |                                                 | $\omega_4$ ring and ring CH deformation |
| 1254 (m)                    | 1247 (m)                                 | 1246 (w)                                        | NH bending and CN stretching |
| 1310 (w), 1340 (s)          | 1309 (w), 1338 (s)                       | 1333 (m)                                        | Ring CH in-plane bending |
| 1417 (w), 1441 (w)          | 1432 (w)                                 | 1401 (w),1427 (w)                              | $\omega_3$ ring puckering vibration; aromatic CH bending |
| 1487 (w)                    | 1486 (w)                                 | 1478 (w)                                        | CH in-plane and NH in-plane bending |
| 1544 (m)                    | 1548 (m)                                 | 1565 (s)                                        | NH in-plane bending |

Letters in parentheses refer to the strength of the peak relatively to the spectrum baseline: vs = very strong, s = strong, m = medium, w = weak. The Greek letters $\nu$ and $\delta$ describe stretching and bending modes respectively.

**Table S3.** Peak assignment for Raman spectra as described in the literature,$^8,^9$ for neat PMPI synthesized by IP at a static liquid-liquid interface, and for PMPI component in composite obtained by ISIP.
| Wavenumber | Wavenumber | Wavenumber | Description |
|------------|------------|------------|-------------|
| 1580 (m)   | 1581 (m)   |            | Amide II vibration, δ(NH) and ν(CN) |
| 1603 (m)   | 1601 (m)   | 1604 (m)   | ω_2 (aromatic ring) CC vibration |
| 1651 (m)   | 1649 (m)   | 1639 (m)   | Amide I (C=O) stretching vibration |

Letters in parentheses refer to the strength of the peak relatively to the spectrum baseline: vs = very strong, s = strong, m = medium, w = weak. The Greek letters ν and δ describe stretching and bending modes respectively.

**S.5 Comparison of PMPI obtained by ISIP with other polymer systems**

**Figure S2.** Polymers which feature amorphous sheath formation in presence of CNTs. Green functional groups have the potential to interact with CNTs through π-interaction.
S.6 References

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