Selective Intercalation of Polymers in Carbon Nanotubes
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A room-temperature, open-air method is devised to selectively intercalate relatively low-molecular-weight polymers (≈10–100 kDa) from dilute, volatile solutions into open-end, as-grown, wettable carbon nanotubes with 50–100 nm diameters. The method relies on a novel self-sustained diffusion mechanism driving polymers from dilute volatile solutions into carbon nanotubes and concentrating them there. Relatively low-molecular-weight polymers, such as poly(ethylene oxide) (PEO, 600 kDa) and poly(caprolactone) (PCL, 80 kDa), were encapsulated in graphitic nanotubes as confirmed by transmission electron microscopy, which revealed morphologies characteristic of mixtures in nanoconfined pharmaceutically relevant systems. Whereas a large number of flexible polymer molecules can conform to enter these nanotubes, larger macromolecules (≈1000 kDa) remain outside. The selective nature of this process is useful for filling nanotubes with polymers and could also be valuable in capping nanotubes.

Introduction
Carbon nanotubes (CNT) not only are promising for future technological applications but also offer an intriguing platform for fundamental research.1 Filling carbon nanotubes with low-molecular-weight fluids or particles is a challenge faced in numerous applications of nanofluidics, including lab-on-a-chip devices, molecular separation (including DNA), drug delivery, dialysis, and so forth.2–7 Early successes in this area involved the encapsulation of molten materials (liquid metals, salts, and oxides).8,9 More recent studies reported the filling of CNTs with aqueous fluids10–13 and organic dopants.14 Advancements in the capillary filling of nanotubes have, in turn, facilitated the successful entainment of nanoparticles in CNT channels.15,16 CNT channels represent themselves as a particular example of nanonanopores. Recent work in this area includes pressure-induced and thermally induced infiltration by water.17,18 These developments inspired efforts to trap polymer macromolecules into CNT channels. The first successful experiments on filling carbon nanotubes with polymers were reported by Liu et al.,19 who employed supercritical CO2, an excellent solvent, to encapsulate polystyrene into multiwalled CNTs with outer diameters of 40–50 nm and lengths of 2–3 μm. The energetics and electronic structure of a polyacetylene chain inside a carbon nanotube were examined theoretically.20 Preliminary experiments on the polycacetylene/CNT system have also been carried out.21 Steinmetz et al.22 reported the preparation of poly(N-vinyl carbazole) or polypyrrole in multiwalled CNTs using supercritical fluid impregnation. The above-mentioned studies have shown that polymer encapsulation in CNT channels is feasible using a two-step process. In the first step,23 supercritical CO2 carries the monomer/initiator components into the CNT cavities. After the removal of CO2, the monomers are then polymerized at a suitable temperature, resulting in polymer/CNT composites. Whereas in principle the supercritical fluid method can be adapted for many other polymers, the procedure involves elevated pressures (≈100 bar), thus posing significant challenges.

This letter describes and demonstrates a transport-based, room-temperature, open-air method of filling untreated (as-grown) hydrophilic CNTs with different flexible polymers. Depending on the size of the polymer macromolecules, the procedure can be used for selective intercalation, wherein high-molecular-weight polymers do not enter the CNT channel but lower-molecular-weight polymers do. In addition to the experimental methods, a theoretical model is also presented to describe the physical transport mechanism believed to be responsible for the selective filling of CNTs with different polymers.

Experimental Methods and Results
Consider a wettable carbon nanotube submerged in dilute polymer solution (Figure 1). The nanotube initially is void of any polymer. Through capillary filling, the polymer molecules (if small enough) will be entrained in the cavity by the wettability-driven flow of the solvent. For linear flexible polymer molecules, their radius of gyration $R_g$ varies approximately in the range of $10–100$ nm for molecular weights in the range of $1–1000$ kDa.23 Consequently, for 100-nm-
Figure 1. Carbon nanotube immersed in dilute polymer solution. The polymer macromolecular coils are indicated as dark dots dispersed in a liquid solvent (gray medium).

diameter nanotubes (2a = 100 nm, 2L is on the order of several micrometers), flexible macromolecules with molecular weights of 10–100 kDa should fit in the cavity, whereas those with weight on the order of 1000 kDa should be incapable of entering. In the case of an evaporating solvent, the concentration of polymer molecules around the CNT would gradually increase as the solvent evaporates. In turn, the resulting concentration gradients would drive (by diffusion) polymer molecules toward the CNT interior. In principle, these polymer concentration gradients can be sustained throughout the entire process until all of the solvent has been removed from the CNT surroundings. Diffusion coefficients of polymer macromolecules with molecular weight M vary as $D_p \propto M^{-1.2}$ in dilute solution at the temperature (where polymer macromolecules behave almost as ideal chains), or $D_p \propto M^{-3.5}$ for dilute solutions with excluded volume, or $D_p \propto M^{-2}$ in the concentrated reptation regime. In all cases, the diffusion-driven supply of smaller molecules is faster. To this end, it seems feasible that during the transient stages, diffusion can be used to enrich the CNT interior in low-molecular-mass polymers dissolved in volatile solvents. Moreover, because the polymer concentration gradients are self-sustained as a result of solvent evaporation, the polymer content inside CNTs could reach almost 100%, even though the initial solution is dilute or semidilute. It is emphasized that in the symmetric situation depicted in Figure 1 with both CNT ends submerged in polymer solution, no polymer entrapment in the CNT can occur by wettability-driven flow (which occurs only in the beginning of the process) or by the flow caused via evaporation near a triple contact line because during most of the filling process the CNT is fully filled by solution. The above-mentioned diffusion-driven mechanism is demonstrated experimentally below.

Commercial, as-grown, highly graphitic (multiwalled) carbon nanotubes (PR-24, Pyrograph III) were employed in this study. The CNTs, which also had some amorphous carbon on their surface, were filled with polymer deposits by the end of the drying process. The substrate porosity facilitated the filling process the CNT is fully filled by solution. The above-mentioned diffusion-driven mechanism is demonstrated experimentally below. In other experiments, as-received CNT powders were submerged in polymer solution. Therefore, initially these nanotubes were empty and are referred to as dry CNTs. Five dilute or semidilute polymer solutions were prepared: (i, ii) deionized water at 0.5 wt %, and less than 5% moisture. The suspension was sonicated for 1 h to eliminate aggregates. Nanotubes after sonication probably contained some water and are referred to as prewetted CNTs. This thin film evaporated rapidly, causing rising polymer concentrations around the CNTs. These concentrations supported polymer diffusion into the CNTs, in turn enriching polymer content in the CNT interior.

A JEOL-3010 transmission electron microscope operating at 300 kV was employed to visualize the CNT interiors at high resolution. The thin layer of dried polymer covering the CNTs allowed an examination by electron microscopy, which was used to evaluate the effectiveness of the polymer filling process. The effect of polymer molecular weight on the intercalation process was investigated first using dry CNTs. The experiments showed that nanotubes submerged into dilute solutions of relatively low-molecular-weight PEO (600 kDa in water) or PCL (80 kDa in MC) were filled with polymer deposits by the end of the drying process. This outcome is consistent with the fact that the radii of gyration of these polymer macromolecules are smaller than the CNT radii. Being supplied by diffusion to the open ends of the CNTs, these molecules proceeded into the CNTs and accumulated there. Various morphologies of the encapsulated polymer deposits are shown in the TEM micrographs of Figure 3a–c. In the tight confinement of the CNTs in Figure 3, polymer molecules are experiencing strong intermolecular interactions in the bulk, as well as with the CNT walls. These interactions tend to condense the polymer material, whereas the entropy-related diffusion process tends to make the material homogeneous. As a result of the competition between these two mechanisms, the dissolved polymer can experience an internal instability with characteristic scales on the order of 10 nm, similar to spinodal decomposition. The instability should result in characteristic deposit patterns with length scales on the order of the CNT inner diameter. The presence of this instability was confirmed by electron microscopy.
by the dried polymer patterns seen in Figure 3a–c. However, this instability and the associated cellular dried polymer patterns were absent outside the CNTs, where the dried polymer deposit appeared uniform when observed in the TEM. The morphological differences of the polymer deposits across the CNT walls facilitated the distinction between the polymer masses inside and outside the CNT. It is noted that the encased PEO patterns seen in Figure 3 closely resemble those observed in the polystyrene/CNT system of Liu et al. However, the filling in the latter study was done by means of supercritical fluid processing (elevated pressure) and subsequent polymerization (elevated temperature), whereas in the present study, the filling was done by diffusion at room temperature and pressure.

At higher PEO molecular weight (2000 and 4000 kDa), where the polymer molecule radii of gyration become comparable to the CNT diameter, polymer macromolecules are continuously supplied to the open ends of the CNTs by diffusion (albeit slower than those with lower molecular weight) but have difficulty penetrating the CNT cavity. As a result, in the case of 2000 kDa PEO, much less polymer could be found deposited inside the CNTs (Figure 4a). At yet higher PEO molecular weight (4000 kDa), even less polymer was found inside the CNTs (Figure 4b). The PEO volumes found deep in the CNT channels in the 2000 and 4000 kDa cases were attributed to lower-molecular-weight fractions present in polydisperse polymers. These lighter molecules with a radius of gyration smaller than the channel radius, \( R_g < a \), were able to penetrate the CNTs, whereas the higher-molecular-weight components with \( R_g > a \) were deposited near the CNT ends (Figure 4c,d) or mostly remained outside. The polymer plugs formed near the CNT ends (Figure 4c,d) could effectively seal the CNTs. In this context, the CNTs acted as selective macromolecule separators allowing the lower-molecular-weight fractions into their cavity while keeping the higher-molecular-weight components outside.

Prewetted CNTs that were brought into contact with PCL solutions in MC, which is miscible with water, were also filled with polymer along their full length (Figure 5a,b). In this case, the filling process should initially involve the rapid diffusion of water molecules (much smaller than PCL molecules) from the prewetted nanotube cavity (if still not evaporated) and the rapid diffusion of MC molecules (also much smaller than PCL molecules) into the CNT. Later on, the diffusion of relatively larger PCL macromolecules (but small enough to enter the CNT channel) brings them without hindrance into the CNTs, which are already filled with MC.

The reported results are significant because polymer-filled nanotubes could have numerous applications in composites, flat panel displays, sensors, and so forth. In addition, the selective nature of the filling may be used to cap (cork) CNTs with large macromolecules that cannot enter the CNT cavity and deposit at the tube end, thus blocking access to its interior. Capping of CNTs filled with a liquid has applications in drug delivery. The unique advantages of this technique (room temperature, open-air processing, single-step, low cost) are very attractive for DNA (e.g., lambda bacteriophage

Figure 3. Relatively low-molecular-weight PEO deposits inside CNTs. They were obtained by dispensing 0.01 wt % PEO (600 kDa) in deionized water over dry CNTs. Three different dried polymer patterns are displayed in the TEM micrographs: (a) pea pod, (b) foam, and (c) dispersed bubbles.

Figure 4. Transmission electron micrographs of higher-molecular-weight PEO deposits inside CNTs. They were obtained by dispensing 0.01 wt % PEO in deionized water over dry CNTs. (a) PEO, \( M_w = 2000 \) kDa and (b–d) PEO, \( M_w = 4000 \) kDa. The detail in d is an enlargement of the marked area in c.

Figure 5. Transmission electron micrographs of PCL deposits inside CNTs. They were obtained by dispensing PCL (80 kDa) in MC over prewetted CNTs: (a) 0.1 wt % solution and (b) 1 wt % solution.

DNA typically used in microfluidic experiments, protein and virus segregation by molecular weight, and encapsulation in CNTs, with potential applications in nanobiotechnology.

Theoretical Analysis and Results

A theoretical analysis was performed to examine the feasibility of the diffusion-based transport mechanism believed to be responsible for the selective filling of CNTs with different polymers. For the system shown in Figure 1 (CNT length 2L, diameter 2a) and because the characteristic size 2a of the spread out droplet (Figure 2) is much larger than 2L, the diffusion process in the vicinity of the nanotube open end can be approximately considered to be spherically symmetric. Then, the polymer concentration \( C_{p,d} \) in the spread out droplet is governed by the following quasi-steady-state diffusion equation

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dC_{p,d}}{dr} \right) = 0 \quad r = \infty, \quad C_{p,d} = C_{p,d0}
\]

\[
C_{p,d} = C_{p,t}
\]

where \( r \) is the radial spherical coordinate centered at the nanotube midpoint, \( C_{p,d0} \) is the polymer concentration in the droplet far from the nanotube, and \( C_{p,t} \) is the polymer concentration inside the nanotube. Note that in the first approximation we assume the polymer concentration inside the nanotube to be uniform. This assumption is valid because possible polymer diffusion inside a CNT is not in the Knudsen regime. Indeed, the mean free path for these macromolecules that can enter a CNT, \( R_f \), is small and obviously \( R_f < a \) and obviously \( R_f \ll L \), which is equivalent to a small Knudsen number and thus ordinary diffusion. The formation of the cellular nanostructures seen inside CNTs in Figures 3 and 5 is attributed to the action of intermolecular forces in addition to diffusion and could be the result of a subsequent spinodal decomposition step after a uniform deposit has filled the tube.

If the nanotube is initially empty, then it will be almost immediately filled with the solvent. Then, the diffusion of the high-molecular-weight polymers can bring them inside the nanotube. Given the concentration distribution following from eq 1, the corresponding polymer flux into the nanotube is given by \( J = 2\pi a^2 D_p(C_{p,d0} - C_{p,t})/L \), where \( D_p \) is the polymer diffusion coefficient in the solvent. Then, the lump mass balance for the nanotube yields the following equation for \( C_{p,t} \):

\[
\frac{dC_{p,t}}{dt} = \frac{D_p}{L^2}(C_{p,d0} - C_{p,t})
\]

Polymer concentration \( C_{p,d0} \) in eq 2 varies with time as a result of solvent evaporation only because polymer losses into the CNT are negligibly small. The surface distribution of the evaporation rate of a sessile droplet shaped as a spherical segment with base radius \( A \) is given as \( j_{ev} \approx 0.1 D_c c_A, \) where \( j_{ev} \) and \( c_A \) are the normal component of the solvent vapor flux and the saturated vapor concentration at the spread out liquid surface, respectively, and \( D_c \) is the diffusion coefficient of solvent vapor in air. Then, at any instant \( t \), the solvent mass in the spread out liquid is given by \( M_s \approx M_{d0} - KD_c c_A, \) where \( M_{d0} \) is the initial solvent mass and \( K = 2\pi(0.1) = 0.628 \). However, when the polymer solution is considered to be a thin, uniform film, \( J_{p} \approx D_p c/A, \) where the diffusion length scale is \( l = nL \) and \( K = \pi nL. \) The corresponding polymer concentration in the drop \( C_{p,d0} \) is given by

\[
C_{p,d0} = \frac{M_p}{M_p + M_{d0} - KD_c c_A}
\]

where \( M_p \) is the polymer mass in the entire liquid volume; \( M_p \) does not change in time because the losses into the CNT are negligible small. It is important to note that polymer solution absorption by the porous substrate is assumed to be over at this stage and polymer concentration in the spread out drop is growing only because of evaporation from the free surface. Nonetheless, ongoing infiltration into the porous substrate could be easily incorporated into the model without affecting the result qualitatively.

By substituting eq 3 into eq 2, we deduce the following problem for \( C_{p,t} \):

\[
\frac{dC_{p,t}}{dt} + \frac{2}{\tau_{diff}} C_{p,t} = \frac{2}{\tau_{diff}} C_{p,d0} + \left( 1 - (t/\tau_{ev}) \right) \quad t = 0, \quad C_{p,t} = 0
\]

where \( C_{p,d0} = M_p/M_{d0} \) [the initial polymer concentration \( C_{p,d0} = C_{p,d0}(1 + C_{p,d0}) \)], and the characteristic diffusion and evaporation times are given by

\[
\tau_{diff} = \frac{L^2}{D_p}, \quad \tau_{ev} = \frac{M_{d0}}{KAD_c c_A}
\]

The exact solution of eq 4 is

\[
C_{p,t} = \frac{2C_{p,d0}}{\tau_{diff}} \exp(-2t/\tau_{diff}) \int_0^{t/\tau_{diff}} \exp(2t/\tau_{diff}) C_{p,d0} \left( 1 + C_{p,d0} \right) \left( t/\tau_{ev} \right) dt
\]

For \( L \approx 1 \mu m \) and \( D_p \approx 10^{-5} cm^2/s \), the characteristic diffusion time is \( \tau_{diff} \approx 10^3 s \). However, in the experiment \( \tau_{ev} \approx 1 \min \); therefore, \( \tau_{diff} \ll \tau_{ev} \). Then, for \( t \ll \tau_{diff} \), the third term in the denominator inside the integral in eq 6 can be neglected, yielding

\[
C_{p,t} = \frac{C_{p,d0}}{1 + C_{p,d0}} \left[ 1 - \exp(-2t/\tau_{diff}) \right] = \frac{C_{p,d0}}{1 + C_{p,d0}} \left[ 1 - \exp(-2t/\tau_{diff}) \right]
\]

In other words, at short times \( t < \tau_{diff} \), liquid evaporation has no effect while the tube is being filled via diffusion to the level approximately corresponding to the ambient low polymer concentration.

However, at long times \( \tau_{diff} \ll t < \tau_{ev} \), the integral in eq 6 can be evaluated using the asymptotic Laplace method, and the resulting expression for the polymer concentration in the nanotube becomes

\[
C_{p,t} = \frac{1}{1 + C_{p,d0} - (t/\tau_{ev})}
\]

A comparison of eq 8 with eq 3 reveals that at this stage the polymer concentration in the CNT resembles that in the drying droplet.


The evaporation process continues until \( t = \tau_{ev} \) when the solvent is fully evaporated. Therefore, the maximum value of the polymer concentration inside the nanotube can reach \( C_{p,\text{max}} = 1 \) (i.e., the diffusion process, which is permanently sustained by the growing concentration of the polymer in the solution, as a result of solvent evaporation, can raise the polymer concentration in the nanotube to almost 100%). In reality, complete filling is not attained, with foamlike cellular structures eventually forming inside the CNT (Figures 3 and 5). These patterns are consistent with the results reported in a separate study\(^1\) where the condensation of vapor molecules inside carbon nanotubes led to the emergence of similar structures formed by the competition of Brownian diffusion and intermolecular forces (Figures 12 and 13 in ref 13).

It is emphasized that because of the dependence of the polymer diffusion coefficient \( D_p \) on the molecular weight of the polymer (or, in other words, on the radius of gyration \( R_g \)), in the case of polydisperse polymer solutions, the CNT content will not resemble that in the drying droplet at intermediate stages but rather will be enriched in the lighter fraction. However, in the case of \( \tau_{\text{dif}} \ll \tau_{ev} \) at the end of the long intercalation process, all of the polymer fractions whose radii of gyration are less than the CNT channel radius (i.e., \( R_g < a \)) will eventually diffuse into the CNT cavity according to the diffusion mechanism described in this section. Only those fractions with \( R_g > a \) will settle outside the CNT or, at the very best, reach the CNT entrance. Therefore, selective intercalation in the present case (\( \tau_{\text{dif}} \ll \tau_{ev} \)) is not the outcome of the diffusion mechanism itself but is rather due to the physical smallness of the CNT channels as compared to the higher-molecular-weight polymers. Finally, it should be mentioned that for the case of very rapid evaporation (i.e., \( \tau_{\text{dif}} \approx \tau_{ev} \)) the possibility still exists to enrich the CNT content with the lighter polymer fraction because the heavier components would not have adequate time to enter the cavity.

**Conclusions**

We have demonstrated a room-temperature, open-air method to selectively intercalate low-molecular-weight polymers from a volatile solvent solution into wettable graphitic nanotubes of 50–100 nm diameter. Low-molecular-weight polymers, such as PEO and PCL, were encapsulated in CNTs as confirmed by transmission electron microscopy, which revealed foam and pea-pod-like patterns of the dried polymer in the CNT channels.

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