Poly(styrene)-b-Poly(dimethylsiloxane)-b-Poly(styrene)/Single Walled Carbon Nanotube Nanocomposites. Synthesis of Triblock Copolymer and Nanocomposite Preparation

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ABSTRACT

CHEMISTRY

STUBBS, IAN B.S. FORT VALLEY STATE UNIVERSITY, 2003

POLY(STYRENE)-b-POLY(DIMETHYLSILOXANE)-b-

POLY(STYRENE)/SINGLE WALLED CARBON NANOTUBE

NANOCOMPOSITES. SYNTHESIS OF TRIBLOCK COPOLYMER AND

NANOCOMPOSITE PREPARATION

Committee Chair: Ishrat Khan, Ph.D.

Dissertation dated December 2016

Molecular weights of 2,000, 6,000 and 10,000 of silane functionalized atactic polystyrene (aPS) and α,ω-divinyl functionalized polydimethylsiloxane (PDMS) were prepared via living anionic polymerization and bulk anionic ring opening polymerization respectively. Functionalization of the homopolymers was confirmed by FT-IR and ¹H-NMR spectroscopy and their molecular weights were determined via ¹H-NMR end group analysis. A hydrosilylation reaction between the functionalized homopolymers of different molecular weights produced nine polystyrene-\textit{block}-polydimethylsiloxane-\textit{block}-polystyrene (aPS-\textit{b}-PDMS-\textit{b}-aPS) triblock copolymers. Field emission scanning electron microscopy observations revealed the copolymers self-assemble into supramolecular structures. Dynamic Light Scattering measurements show only small
increase in the order of nanometers of its hydrodynamic radius as the individual molecular weights of the homopolymers were increased.

Nanocomposites of the copolymers were prepared by incorporating 1% of oxidized single walled carbon nanotubes (SWNTs) within the aPS-PDMS-aPS matrices via coagulation precipitation. Differential scanning calorimetry (DSC) thermal analysis shows the SWNT interacting with both aPS and PDMS constituting blocks. SWNTs interaction with aPS block either increases the polymer glass transition temperature ($T_g$) by restricting its segmental motion or decreases the $T_g$ by a plasticization effect. Within the PDMS block the SWNTs act as nucleating sites accelerating the crystallization rate of the polymer. This is evident by the appearance of single and double melting endotherms in the DSC thermograms.
POLY(STYRENE)-b-POLY(DIMETHYLSILOXANE)-b-POLY(STYRENE)/SINGLE WALLED CARBON NANOTUBE NANOCOMPOSITES. SYNTHESIS OF TRIBLOCK COPOLYMER AND NANOCOMPOSITE PREPARATION

A DISSERTATION
SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

BY
IAN STUBBS
DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA

DECEMBER 2016
ACKNOWLEDGEMENTS

Above all things on earth and in heaven, with words of appreciation I cannot express, I thank The Holy Trinity, God the Father, God the Son, and God the Holy Spirit whose mercy, love and forgiveness I will always acknowledge and through Whom I can accomplish all things.

My deepest appreciation goes to my family members for their unwavering support and love through the years. This appreciation is also extended to my eternal friend, Marcia Musgrove, whose friendship and patience I will always cherish.

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<td>2K</td>
<td>2,000</td>
</tr>
<tr>
<td>6K</td>
<td>6,000</td>
</tr>
<tr>
<td>10K</td>
<td>10,000</td>
</tr>
<tr>
<td>A/cm²</td>
<td>Ampere per centimeter square</td>
</tr>
<tr>
<td>ar</td>
<td>Aromatic</td>
</tr>
<tr>
<td>AROP</td>
<td>Anionic ring opening polymerizations</td>
</tr>
<tr>
<td>C=C</td>
<td>Carbon-Carbon double bond</td>
</tr>
<tr>
<td>C=O</td>
<td>Carbonyl Functional Group</td>
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<tr>
<td>CGP</td>
<td>Chain growth olefin polymerization</td>
</tr>
<tr>
<td>C–H</td>
<td>Carbon Hydrogen bond</td>
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<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>D₃</td>
<td>Hexamethylcyclotrisiloxane</td>
</tr>
<tr>
<td>D₄</td>
<td>Octamethylcyclotetrasiloxane</td>
</tr>
<tr>
<td>D–Band</td>
<td>Disorder Band</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>FT–IR</td>
<td>Fourier Transformer Infrared Spectroscopy</td>
</tr>
<tr>
<td>GPA</td>
<td>Gigapascals</td>
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</table>
G–Band  Graphitic Band
I_D  Intensity of Disorder Band
I_D/I_G  Ratio of the intensities of the disorder and graphitic bands
I_G  Intensity of Graphitic Band
KOH  Potassium Hydroxide
LAP  Living Anionic Polymerization
M_n  Number average molecular weight
MWNT  Multiwalled Carbon Nanotubes
N  total number of repeating units per polymer chain
NMR  Nuclear Magnetic Resonance
OH  Hydroxyl Functional Group
ρ  Density
PCN  Polymer carbon nanotube nanocomposite
PDMS  Polydimethylsiloxane
Platinum  Pt
Proton  \(^1\)H
Proton NMR  \(^1\)H Nuclear Magnetic Resonance
PS  Polystyrene
PS–SiH  Silyl hydride functionalized Polystyrene
R_h  Hydrodynamic radius
S/m  Siemens per meter
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>SGP</td>
<td>Step growth polymerization (SGP)</td>
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<td>Si–C</td>
<td>Silicon-Carbon bond</td>
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<tr>
<td>Si–H</td>
<td>Silyl hydride</td>
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<td>SMA</td>
<td>Sequential Monomer Addition</td>
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<td>STPE</td>
<td>Styrenic thermoplastic elastomers</td>
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<tr>
<td>tBMA</td>
<td>Tert-butyl methacrylate</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Melting Temperature</td>
</tr>
<tr>
<td>TPa</td>
<td>Tetrapascals</td>
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<tr>
<td>V₂M₄S₂</td>
<td>1,2-divinyl-1,1,3,3-tetramethyldisiloxane</td>
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<tr>
<td>vdw</td>
<td>van der Waals</td>
</tr>
<tr>
<td>v–PDMS</td>
<td>Divinyl functionalized polydimethylsiloxane</td>
</tr>
<tr>
<td>W/K·m</td>
<td>Kelvin per meter</td>
</tr>
<tr>
<td>χ</td>
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CHAPTER I
INTRODUCTION

Polymer carbon nanotube nanocomposites (PCNs) are composite materials that combine the processability and versatility for product applications of polymers with the high mechanical strength, Young’s modulus, excellent electrical and thermal conductivities and thermal stability of carbon nanotubes (CNTs). They are considered to be the next innovative materials because of their light weight, durability, versatility and multifunctional characteristics. Several potential applications have been envisioned for PCNs in wide range of industries, including but not limited to electronics, aerospace and biomedical/bioengineering.

PCNs are normally prepared from homopolymers while copolymers are used for functionalizing CNTs to facilitate their dispersion and improve their stability in diverse solvents. Currently, block copolymers are being studied as potential host for CNTs.\(^1\) Copolymers possess properties intermediate between the properties or unique properties different than those of the corresponding homopolymers. This is the principle advantage for creating PCNs from copolymers. However, a possible complication to using block copolymers as a host for CNTs is the immiscibility between the constituent polymer blocks arising from their different physical morphologies.
This will cause the copolymer to display the characteristic of each homopolymer. For instance, diblock copolymers composed of two incompatible polymers will exhibit two separate glass transition temperatures corresponding to each of the polymer segments. The immiscibility of the segments, which results in microphase separation, may also cause the CNTs to have a higher affinity for a specific microphase in the block of the copolymer matrix. If this occurs, it may limit the impact of SWNTs on the properties of the entire macromolecule and provide an advantage in that locating the CNTs in one microphase will permit the development of processible functional composite materials with interesting properties.

To investigate if in fact CNTs prefer to interact or interact to a greater degree with a particular polymer block of a copolymer, carboxyl functionalized single walled carbon nanotubes (SWNTs) are incorporated within the triblock copolymer matrix polystyrene-\textit{block}-polydimethylsiloxane-\textit{block}-polystyrene (PS-\textit{b}-PDMS-\textit{b}-PS) (Figure 1.1).

![Chemical structure of PS-b-PDMS-b-PS triblock copolymer](image)

Figure 1.1 Chemical structure of PS-b-PDMS-b-PS triblock copolymer.
PS-\textit{b}-DMS-\textit{b}-PS is an ideal candidate to test this hypothesis, because it is comprised of the two of the most immiscible polymers, i.e. polystyrene (PS) and polydimethylsiloxane (PDMS). PS is a rigid thermoplastic with a physical state that varies from crystalline to amorphous glass depending on its tacticity and has a glass transition temperature around 100 °C. PDMS is semi-crystalline at very low temperatures but highly flexible at room temperature with an amorphous state varying from oils to grease to solid elastomers, depending on its molecular weight and degree of crosslinking. SWNTs have been incorporated into PS to enhance its mechanical strength and impart electrical conductivity.\textsuperscript{2-4} Dispersing SWNTs in polydimethylsiloxane (PDMS) creates an electrically conductive material useful for applications requiring flexible microelectronic circuitry.\textsuperscript{5,6} If SWNTs can be successfully disperse uniformly throughout the entire PS-\textit{b}-PDMS-\textit{b}-PS matrix, it will create an electrically conductive nanocomposite material capable of substantial stretching and bending with applications in engineering flexible devices and sensors,\textsuperscript{6,7} microelectromechanical systems\textsuperscript{9} and strain gauges.\textsuperscript{10}

SWNTs’ interaction with PS-\textit{b}-PDMS-\textit{b}-PS occurs via hydrophobic contact with the copolymer non-covalently wrapping around the cylindrical SWNTs. PS–SWNT interaction also occurs through π–π stacking between the phenyl rings of the PS and the extensive π conjugated network of the SWNT. The strength of the PS-\textit{b}-PDMS-\textit{b}-PS/SWNTs interactions depends on the molecular weight, tacticity and physical characteristic (flexibility, solubility, etc.) of the polymer blocks. The mentioned factors will play a crucial role in determining, if SWNTs has a preferential molecular interaction with PS and PDMS. Any preferential SWNT interaction or the absence thereof will cause
changes in the phase transitional temperatures of the constituent PS and PDMS blocks which can be detected by differential scanning calorimetry (DSC) thermal analysis. For PS SWNTs will either decrease the glass transition temperature by a plasticization effect or increase it by restricting the segmental mobility of the polymer chains. SWNTs can either increase or suppress the crystallization of PDMS.
2.1. Living Anionic Polymerization

2.1.1. General Overview

Szwarc initially defined a living polymerization system as a polymerization reaction proceeding in the absence of the kinetic steps of chain breaking reactions such as irreversible termination and irreversible chain transfer,\textsuperscript{11-13} a feature first observed by Ziegler.\textsuperscript{14} Szwarc later modified this definition stating “a polymerization is living when the resulting polymer retains its integrity for a sufficiently long time to allow the operator to complete a task, whether a synthesis or any desired observation or measurement. Even in that time some decomposition or isomerization may occur, provided it is virtually undetectable and does not affect the results.” Living anionic polymerization (LAP) became the first living polymerization system and presently is the most used method for preparing living polymers. LAP is a chain growth polymerization where the propagating species is a carbanion formed by the initiator undergoing nucleophilic addition to the monomer. Similar to other chain polymerization mechanisms, it involves the elementary steps of initiation and propagation. The propagating anionic centers remain active after 100% of the monomer is consumed and incorporated into the polymer chain.
The general mechanism for LAP is illustrated in Figure 2.1

![Diagram of the general mechanism for living anionic polymerization.](image)

Figure 2.1. General mechanism for living anionic polymerization.

Upon the addition of more monomer, the polymerization will resume and the polymer chain will grow further in molecular weight. If the system is sufficiently absent of active hydrogen sources such as water, acids or alcohols, atmospheric components such as carbon dioxide and oxygen and other adventitious molecules capable of reacting with the active chain ends, termination will not occur spontaneously for some time. However, termination can occur by deliberate addition of electrophilic reagents or functional groups that undergo proton exchange with the living system. LAP is the most effective method for synthesizing functional polymers and block copolymers. It is the premier polymerization mechanism for facilitating the studies of polymerization kinetics and for the preparation of polymers of predetermined narrow molecular weight distributions and predictable molecular weights. Furthermore, LAP allows the synthesis of copolymers of various architectures and provides control of the microstructure e.g. in polydienes.\(^\text{15}\)
The living feature of the propagating chains provides a significant degree of control and versatility in polymer synthesis. With monofunctional initiators, the number of polymer chains that are produced is equal to the number of initiator molecules consumed. Therefore, it is easy to control the number average molecular weight (Mₙ) of the polymer within a desired range, through the ratio of the weight of the monomer consumed to the moles of the initiator. The expected Mₙ can be calculated, as shown in the equation below.

\[ M_n = \frac{\text{moles of monomer consumed}}{\text{moles of the initiator}} \]  

Equation 1

2.1.2. Synthesis Capabilities: Copolymerization and Chain-end Functionalization

A significant feature of LAP is its capability to synthesize block copolymers via sequential monomer addition (SMA) and polymer with various functional end groups. SMA can be used to prepare diblock copolymers of A–B composition, triblock copolymers with A–B–A and A–B–C sequence, and multiblock copolymers with complex architectures such as star-shaped, comb-shaped and dendritic polymers. Hadjichristidis et al. gave three principle conditions that must be fulfilled to successfully synthesize and design of well-defined copolymers via SMA. The three principles conditions are;
1. **Carbanionic Stability:** SMA directly depends on the stability of the active carbanionic chain ends. Thus, the carbanion formed by the second monomer must be more, or at least equally, stable or more stable than the one derived from the first monomer. For example, a block copolymerization starting with tert-butyl methacrylate (tBMA) followed by the addition of styrene will fail. Firstly because the crossover step (efficient transfer of the carbanionic active sites to the second monomer) is not controlled since the methacrylate anion is more stable than the styryl anion. Secondly, the polystyryl anions will attack the ester function of tBMA, resulting in branching and termination. Therefore, proper sequence of monomers is of great importance. One has to start with the polymerization of the monomer, which has the least stable anion. Carbanion stability can be determined by its pKₐ values.

2. **The Rate of The Crossover Reaction:** For an efficient crossover, the reaction rate for the initiation of the second monomer by the anion of the first monomer must be higher than its rate of propagation. This ensures narrow molecular weight distribution for the second polymeric block and complete consumption of anion of the first monomer. Incomplete consumption of the first monomer propagating anion will result in formation of a homopolymer of the first monomer.
3. **Purity**: The purity of the second monomer must be high. Otherwise, partial termination of the living anions of the first monomer can take place leading to the presence of its homopolymer in the final product. Additionally, loss of molecular weight and composition control of the second block and of the whole copolymer will occur, because the concentration of the active centers will be decreased.

The first condition applies for all diblock copolymerizations and only for some cases of triblock copolymerization. In the other cases SMA is ineffective for the anionic synthesis of triblock copolymers regardless of the order of sequence in which the monomers are added. An example of this limitation is observed in the preparation of the PS-PDMS-PS triblock copolymer. The living styryl anion formed from the anionic polymerization of styrene can successfully initiate the ring opening polymerization of hexamethyldicyclotrisiloxane (D₃). However, the resulting living silanolate anion is far less basic than the styryl anion and therefore is not reactive enough to initiate the polymerization of a second batch of styrene to produce the PS-PDMS-PS triblock. Such a problem can be overcome by using alternative methods other than the three-step sequential monomer addition. These alternative methods are difunctional initiation follow by sequential monomer addition (Figure 2.2a), the coupling of two telechelic polymers (Figure 2.2b) and the coupling of a telechelic diblock polymer with a telechelic polymer (Figure 2.2c).
Figure 2.2. Reaction scheme showing the alternative methods for preparing triblock copolymer. X and Y represents functional groups capable of undergoing a coupling reaction.

(a) Difunctional initiation follow by sequential monomer addition

\[
\text{macro dianion} + nA \rightarrow \text{triblock copolymer}
\]

(b) Coupling of two telechelic polymers.

\[
\text{Difunctionalized polymer} + \text{Monofunctionalized polymer} \rightarrow \text{telechelic diblock copolymer}
\]

(c) The coupling of a telechelic diblock polymer with a telechelic polymer

Figure 2.2. Reaction scheme showing the alternative methods for preparing triblock copolymer. X and Y represents functional groups capable of undergoing a coupling reaction.

Telechelic polymers are chain-end functionalized homopolymers with one or more functional groups, which can further react with other functionalities. Several important chain-end functionalization reactions in anionic polymerization are illustrated in Figure 2.3.
Figure 2.3. Chain end functionalization reactions with electrophilic reagents

The chain end functionalized telechelic polymers are valuable macro-precurors and can undergo further reactions which are divided into three categories: (i) further polymerization of macromonomer; (ii) coupling with multifunctional electrophilic reagents to form special structures such as multi-arm star branched polymers;
(iii) coupling with two homopolymers, each terminated with a reactive functional group yielding block or graft copolymers. The last reaction is useful in preparing triblock copolymers that cannot be formed by SMA. However, the coupling reaction between reactive functionalities is never complete and purification is required to remove the uncoupled homopolymers to obtain the pure block copolymer.

2.2 Anionic Ring Opening Polymerization

Anionic ring opening polymerizations (AROP) follow the same sequential initiation, propagation and deliberate (nonspontaneous) termination, mechanistic steps as in LAP. They involve the formation and propagation of anionic centers from the ring opening reactions of heterocyclic monomer molecules induced by the nucleophilic attack of anionic initiators or anionic chain ends. Figure 2.4 illustrates a general scheme for AROP for cyclic monomers.

\[ \text{X} = \text{carbon silicon; Y} = \text{oxygen, nitrogen, sulfur, etc.}\]

Figure 2.4. General anionic ring open polymerization mechanism.
AROP mechanisms can proceed either by chain (addition) growth olefin polymerization (CGP), step growth (condensation) polymerization (SGP), or sometimes displays features of both.\textsuperscript{20-22} It is similar to CGP in that only monomer adds to the growing chains in propagation and polymers of predictable molecular weights can be prepared. Like SGP sometimes AROP eliminates small molecules upon the addition of a monomer. However, AROP differ from both SGP and CGP in one important aspect. Comparing the molecular structure of the monomer and repeating unit of the corresponding polymer reveals the bonding sequence is the same for both in AROP. In contrast, the bonding sequence is different in SGP due to the condensation of small molecules and CGP due to the loss of unsaturation.

AROP of cyclosiloxanes is the principal method of preparation for linear polysiloxanes or silicones. Polymethylsiloxane (PDMS), the most well-known silicone, is produced either by alkyllithium initiated polymerization of the strained cyclic trimer $D_3$ or the base catalyzed polymerization of the unstrained cyclic tetramer octamethylcyclotetrasiloxane ($D_4$). The latter method is the preferred synthetic route for the industrial production of PDMS and its functionalized derivatives. Consequently, the reaction kinetics and mechanism for the bulk ring opening reaction of $D_4$ catalyzed by potassium hydroxide (KOH) have been extensively review in literature\textsuperscript{23-27}. The KOH catalyzed AROP of $D_4$ overall is classified as an addition polymerization, but its propagation step is more complicated, involving multiple side reactions. Figure 2.5 shows the mechanistic route for the preparation of PDMS via KOH catalyzed AROP of $D_4$ and its functionalization by a siloxane end-blocker.
Figure 2.5 AROP mechanism of D₄

KOH is a non-transient catalyst, meaning it does not thermally decompose to inert by-products at elevated temperatures. Thus, it has to be neutralized and removed to prevent unwanted reactions. The similar reactivity of the siloxane bond (Si–O) in D₄, the siloxane derived end-blocker and the propagating polysiloxane chains makes their Si–O bonds susceptible to attack by a siloxanolate anion. This allows intermolecular and intramolecular chain transfer reactions to occur between the different siloxane compounds. In contrast the silicon–carbon (Si–C) bond is a covalent bond of low polarity and, therefore will not undergo any chain transfer reactions. The most useful intermolecular reaction involves the termination of species II with a siloxane end-blocker bearing various functionalities to form α, ω-difunctionalized PDMS (III). The Mₙ of the
functionalized PDMS is controlled by the molar ratio of $D_4$ to the end-blocker.$^{28, 29}$ Intramolecular reactions involve a reversible propagation step known as backbiting. Backbiting occurs when an active propagating polysiloxane anionic chain end attacks a Si–O bond at least four repeating units away along its own backbone (Figure 2.6).

![Figure 2.6. Intramolecular (backbiting) reaction of a propagating polysiloxane chain.](image)

The backbiting reverse manoeuvre causes the formation macrocyclic siloxanes of various sizes which can be reinitiated by the catalyst. To limit backbiting it is preferable to conduct the polymerization in bulk rather than in solution. Bulk polymerization provides a greater opportunity for the siloxanolate anion to encounter a cyclic monomer rather than a propagating chain. After deactivation and removal of the KOH catalyst the macrocyclic siloxanes can be removed by devolatilization, that is vacuum distillation at elevated temperatures. The combination of continuous breaking and reforming of linear and cyclic Si – O bonds through intermolecular and intramolecular reactions produces an equilibrium mixture consisting of 85 – 90 % linear polysiloxane chains and 10 – 15 % cyclosiloxanes.$^{30-32}$
2.3 Hydrosilylation

Hydrosilylation is a cross coupling reaction involving the addition of silicon hydride (Si–H) cross multiple bonds of unsaturated functionalities as shown in Figure 2.7 to create new Si–C and carbon – hydrogen (C–H) bonds. A feature of its mechanism is that the two reactants combine to form a third without producing any by-products.

Figure 2.7. Hydrosilylation coupling reactions between silyl hydride and unsaturated functional groups.
It can proceed by three principal mechanisms: (i) by free radical chain reactions initiated by heat, peroxides, 2,2-azobisisobutyronitrile (AIBN), or under ultra-violet or gamma irradiation; (ii) an ionic mechanism with Lewis acids or other nucleophiles as initiators; (iii) under catalysis by transition metal complexes. Complexes of the transition metals, platinum, rhodium, nickel and palladium, are the most efficient and versatile hydrosilylation catalysts requiring mild reaction conditions. They have excellent compatibility with a wide diverse range of functional groups and their reaction mechanism does not produce by-products from the covalent bonding of two molecules to form a third. For these reasons, they are utilized in the laboratory and industrial synthesis of organosilicon molecular and macromolecular compounds. A significant feature of transition metal catalyzed hydrosilylation is that addition of Si–H to unsaturated bonds follows Markovnikov and anti-Markovnikov rules. The regioselectivity is governed mainly by the transition metal catalyst used. Hydrosilylation catalyzed by platinum and rhodium complexes undergo anti-Markovnikov addition, while palladium complexes favor Markovnikov addition.

Platinum complexes are the most frequently used catalyst for hydrosilylation owing to their effectiveness at relatively low concentrations. Only 0.1 ppm is required to catalyze initiate the reaction. The first platinum catalyzed hydrosilylation reaction was carried out using dihydrogen hexachloroplutinate (IV) hexahydrate (Figure 2.8), and is commonly referred to as Speier’s catalyst.
However, Speier’s catalyst is a potent sensitizer and has a longer induction period because the platinum has to be reduced from an oxidation state IV to zero (Pt (0)) before becoming catalytically active, its use has been quite limited. It was eventually superseded by the safer Karstedt’s catalyst (tris(tetramethyl-1,3-divinylsiloxane) diplatinum). \(^{38}\)

Karstedt’s catalyst consists of a Pt center having an oxidation state of zero coordinated to 1,3-divinyltetramethyldisiloxane ligands by the C = C bonds of the vinyl groups (Figure 2.9).

Figure 2.9. Solvation of Karstedt’s Catalyst
The platinum complex (I) is referred to as the pre-catalyst and upon solvation the ligand is released yielding the more active catalyst form (II). Higher levels of reactivity and product yield are achieved with Karstedts catalyst, because the Pt does not need to undergo reduction prior to becoming active.39

The mechanism of the platinum catalyzed hydrosilylation was proposed by Chalk and Harrod.40,41 The Chalk – Harrod mechanism is shown in Figure 2.10. The mechanism tentatively parallels the organometallic reaction of the hydrogenation of alkenes as it involves the conventional oxidative addition and reductive elimination elementary steps. The mechanism begins with the initial oxidative addition of the silane to the Pt(0) center (1) to generate a Pt(II) species, a hydrido – silyl intermediate complex, which coordinates with an olefin or other unsaturated species (2). The complex undergoes migratory insertion of the alkene into the Pt(II) – H bond (hydrometallation) to give a Pt alkyl –silyl intermediate complex (3). Hydrometallation is the rate determining step in this reaction. Subsequent reductive elimination of the silyl and alkyl ligands forms the hydrosilylation product and regenerates the catalyst to restart the catalytic cycle (4). The Chalk – Harrod catalytic cycle successfully explains the anti-Markovnikov regiochemistry of Pt – catalyzed hydrosilylation. However, the Chalk – Harrod mechanism fails to account for the observed formation of dehydrogenative silylation (vinylsilane) products. A modified version of the Chalk – Harrod mechanism has been proposed to address the observation of vinylsilane products.
Figure 2.10. Chalk-Harrod and modified Chalk-Harrod mechanism.
The modified Chalk – Harrod mechanism steps are similar to the original, except the coordinated alkene preferentially inserts into the Pt – Si (silylmethallation) bond rather than the Pt – H bond to form a β-silylalkyl-hydrido intermediate complex (5) and the C – H bond is formed during the reductive elimination step. Detailed theoretical studies have determined that depending on the transition metal pre-catalyst either the original or modified Chalk – Harrod mechanism reaction pathway is preferred. Sakaki et al, based on their theoretical studies of the hydrosilylation coupling of ethylene and silane derivatives catalyzed by a platinum(0) – bis(phosphine) complex concluded that all Pt (0) catalyzed hydrosilylation reactions undergoes the original Chalk – Harrod mechanism.42

2.4 Block Copolymers of Polystyrene and Polydimethylsiloxane

The majority of polymers are immiscible due to their different physiochemical properties. Consequently, copolymers segregate to avoid intramolecular interaction between its constituting homopolymers. The segregation strength in block copolymers is primarily thermodynamically driven by the product of $\chi N$, where $\chi$ is the Flory–Huggins interaction parameter between block components and $N$ is the total number of repeating units per polymer chain.43, 44 When $\chi N$ is less than 100 the two homopolymers are weakly segregated and if $\chi N$ exceeds 100, the homopolymers are strongly segregated. Block copolymers of PS and PDMS have the most pronounced immiscibility compared to any other block copolymers45, 46 and have the highest $\chi$ value of 0.26. Therefore, they will have the greatest driving force undergo self-assembly and microphase separation.
Self-assembly is the autonomous organization of molecular components into ordered patterns or structures without guidance or management from an outside source. Linear di- and triblock copolymers of PS and PDMS will self-assemble into micellar or lamellar aggregates, when dissolved in solvents that are good solvents for one block and a precipitant or poor solvents for the other. The shapes and size of these aggregates are governed by the relative block lengths (molecular weight), the chemical nature of the blocks and the type of solvent use for the polymer solution preparation. Microphase separation occurs with triblock copolymers of the A – B – A architecture, where the end blocks (A) are short chains of the thermoplastic PS and the midblock (B) is a long chain of the elastomer PDMS. The immiscible PS and PDMS blocks naturally repel each other, but the covalently bond prevents macroscopic phase separation. As a result their microphase separation is spatially limited. To simultaneously minimize the surface interfacial area (contact) between the different blocks and to maximize intermolecular interactions between identical polymer blocks, the triblock copolymer will forms well-defined microdomains within the bulk material. The hard PS end-blocks will form hard spherical glassy microdomains rigidly locked in placed below its $T_g$ of 100°C. They are small, typically 10–30 nm in diameter and well dispersed. The PDMS middle block will form a soft amorphous phase because it’s $T_g$ (-125 to -127 °C) and melting temperature (Tm) (-42 to -48°C) are well below ambient temperature.

The morphology and physical properties will vary between glassy and viscoelastic depending on the ratio of the molecular weight of the homopolymers. If the PDMS is the main constituent, the physical properties of the triblock copolymer should resemble those
of styrenic thermoplastic elastomers (STPE). Here, the minor or discontinuous PS glassy spherical region is dispersed throughout the major or continuous PDMS matrix with each PS end-block of a triblock macromolecule being part of a different glassy domain. At room temperature the hard PS domains act as physical crosslinks anchoring the PDMS phase into a three dimensional network. The weight percentage (wt. %) of the styrene should not exceed 30% so as to ensure the formation of the spherical domains. A schematic illustration of this morphology is shown in Figure 2.1.

![Schematic illustration of PS-b-PDMS-b-PS triblock copolymer morphology](image)

**Figure 2.1.** Morphology of the PS-b-PDMS-b-PS triblock copolymer.

If the PS-b-PDMS-b-PS is heated or dissolved in a solvent the PSt domain will lose its integrity but will reassemble once cooled or the solvent is evaporated. The physical
crosslinked network of the PS-\textit{b}-PDMS-\textit{b}-PS triblock copolymer allows it to be considered as a potential STPE. If the PS segment is the major component, the minor discontinuous PDMS segment will be confined within hard glassy domain. The copolymer will be more rigid and brittle.

The properties of PS-\textit{b}-PDMS-\textit{b}-PS triblock copolymer are an amalgam of the exceptional properties of silicone polymers and polystyrene. The majority of the unique properties stems mainly from features imparted by the PDMS block. Silicons possess excellent thermal and oxidative stability, good gas permeability, low solubility parameter, low surface energy, retention of flexibility at low temperatures, great durability towards weathering and excellent radiation stability.\textsuperscript{48, 49}

2.5 Carbon Nanotubes

Carbon nanotubes (CNTs) are members of the buckminsterfullerenes or fullerenes family, the third allotrope of carbon. The Japanese electron microscopist Sumio Iijima, was officially accredited with their discovery while investigating the soot byproduct formed from the electric arc discharge synthesis of fullerenes.\textsuperscript{50, 51} However, pre-1991 evidence for the existence of CNTs was reported by several scientists almost four decades earlier.\textsuperscript{52-54} Presently, CNTs are considered one of the most promising materials of 21st century that will have a significant impact on future technology.
2.5.1 Structure

CNTs or buckytubes can be visualized as hollow cylinders fabricated by rolling sheets of graphene into a seamless cylinders such that the lattice of the carbon atoms remains continuous around the circumferences. These macromolecules of the carbon atoms typically have diameters ranging from <1 nm up to 50 nm, while they can be up to several millimeters in length. The open tubes may or may not have at least one end capped off by a hemispherical fullerene molecule. The hemispherical fullerenes end caps are made of pentagonal defects in order for curvature to exist. They are very reactive due to curvature strain and are readily destroyed during processing, yielding open tubes. The graphitic sidewall of CNTs has localized imperfections, such as the Stone-Wales (or 7-5-5-7) defect shown in Figure 2.12, sp³ hybridized carbons and spaces in the CNT lattice. Typically around 1–3% of the carbon atoms of a nanotube are located at defective sites.⁵⁵

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Figure 2.12. Stone–Wales (or 7-5-5-7) defect on the sidewall of a nanotube.
During the growing process, depending on the conditions of the synthetic method by which they are formed, CNTs are either produce as single walled carbon nanotubes (SWNTs) or multi-walled carbon nanotubes (MWNTs). SWNTs and MWNT are illustrated in Figure 2.13. As produced SWNTs tend to assemble as crystalline bundles or ropes (Figure 2.14) due to the strong van der Waals forces of attraction (0.5 eV/nm).56

Figure 2.13 Structure of (a) SWNT and (b) MWNT
The rope contains between 20 to 500 individual tubes packed in a two dimensional triangular lattice or hexagonal array with a lattice constant of 1.7 nm.\textsuperscript{57-60} The diameters for SWNTs differ from 0.4 to 3nm with lengths in the micrometers. MWNTs as shown in Figure 2.13(b) consist of a coaxial arrangement of two to as many as fifty concentric SWNTs with interlayer spacing between the individual SWNTs closely matching the spacing between graphene layers in graphite, approximately 0.34 nm or 3.4Å.\textsuperscript{61} MWNTs form highly entangled networks. Depending on the way graphene sheets are rolled, the atomic structure or arrangement of individual CNTs are described as having an achiral or chiral symmetry. The CNT chirality or helicity is defined by the chiral vector (also refer to as the roll-up or circumferential vector) and the chiral angle. Figure 2.15 assists in forming a mental picture how the chiral vector and chiral angle specifies the CNT structure.
Figure 2.15. Rolling a graphene sheet to produce a chiral (5,3) SWNTs. $a_1$ and $a_2$ correspond to the lattice vectors of graphene. OA corresponds to the chiral vector OB and AB' correspond to the translational vector along the tube axis.

The chiral vector $\vec{C}_h$ is calculated by the mathematical equation:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$$  \hspace{1cm} \text{Equation 2}$$

where $\vec{a}_1$ and $\vec{a}_2$ are base cell unit vectors of the hexagonal lattice and correspond to a section of the CNT perpendicular to the CNT axis and n and m, are translational indices that give the number of steps along the unit vector of the hexagonal lattice.
The indices \((n, m)\) are positive integers with values of \((0 \leq |m| \leq n)\). The chiral angle \(\theta\) is the angle formed between vectors \(\vec{C}_h\) and \(\vec{a}_1\) with values in the range of \(0^\circ \leq |\theta| \leq 30^\circ\). It determines the amount of twist in the tube and denotes the tilt angle of the hexagons with respect to the nanotube axis. The axis of the CNT is orthogonal to the chiral vector. Likewise the chiral angle can also be calculated from the indices \((n, m)\) as follows:

\[
\theta = \cos^{-1} \left( \frac{\vec{C}_h \cdot \vec{a}_1}{|\vec{C}_h||\vec{a}_1|} \right) = \cos^{-1} \left( \frac{2n+m}{2\sqrt{m^2+nm+n^2}} \right)
\]  

Equation 3

The chiral angle \(\theta\) give rise to three possible geometric orientations or helicities for the carbon atoms of the CNTs, differentiated by their electronic properties. Two limiting cases, corresponding to the achiral CNTs, exist where the chiral angle is at \(0^\circ\) and \(30^\circ\). The orientation of these limiting cases are referred to as armchair when \(\theta = 30^\circ\) and \(n = m\) and zig-zag when \(\theta = 0^\circ\), \(n > 0\) and \(m = 0\). All other orientations are referred as chiral CNTs with values \((0 < |m| < n, 0^\circ < \theta < 30^\circ)\). Figure 2.16 illustrates the zigzag \((n, 0\) or \(0, m)\), armchair \((n,n)\) and chiral \((n,m)\) structures of CNTs.
Figure 2.16. Helicities of (a) Armchair \((n = m)\), (b) zigzag \((n, 0)\) and (c) chiral \((n, m, m \neq 0)\) CNTs.

2.5.2 Properties

CNTs are known for their intrinsic high mechanical, thermal and electrical macroscopic properties, which are strongly anisotropic or directionally dependent. This unique combination of exceptional properties results from the CNTs highly ordered atomic arrangement, extensively conjugated \(\pi – \pi\) system, helicity (chirality), and individual dimensions.

CNTs are among the strongest materials yet discovered in terms of tensile strength, elastic modulus (stiffness) and hardness. Their physical strength is attributed to the strong covalent \(sp^2\) carbon – carbon \((C=C)\) hybridized bonds between the individual carbon atoms, which are coiled into a cylinder. The atomic arrangement enables CNTs to
function as one whole macromolecule. This means it does not have the weak spots found in other materials, such as the boundaries between the crystalline grains that form steel. It has been reported that CNTs have a tensile strength about 10–100 times greater than that of the strongest steel alloy of the same diameter, but only one-sixth of the weight, and a density half that of aluminum\(^6^2\). The sp\(^2\) bonds are stronger than the sp\(^3\) bonds found in diamond, making CNTs about 20\% harder and one of the hardest natural occurring materials.

Several experimental studies have been carried out to determine the tensile strength and elasticity modulus of individual CNTs\(^6^2, 6^3\). One of the most accurate in situ tensile test on MWNTs and bundles of SWNTs were performed by Yu et al who conducted stress-strain measurements using a “nanostressing stage” operated inside a scanning electron microscope\(^6^4, 6^5\). Their experimental results revealed the elastic modulus for the outermost layers of MWNTs ranged from 270 to 950 gigapascals (GPa) and the tensile strength ranged from 11 to 63 GPa at fracture strains of up to 12\%. For the rope assembly of SWNTs an average tensile strength of 13 to 52 GPa and average elastic moduli of 320 to 1470 GPa were reported, assuming only the outermost tubes of rope assembly carried the load. Using an atomic force microscope Salvetat et al calculated an average modulus of 810 ± 41.0 GPa for MWNTs\(^6^6\) and 1 tetrapascal (TPa) for SWNTs\(^6^7\). All the experimental studies of mechanical properties concluded that the strength of CNTs depends on the number of defects, as well as the interlayer interactions in MWNTs and bundles of SWNTs.
Besides their amazing mechanical strength CNTs have exceptional flexibility. When subject to stress in the axial direction carbon atoms in a specific part of CNT cylinder undergo a Stone-Wales transformation to alleviate stress upon tensile failure. The Stone–Wales transformation is a reversible diatomic arrangement involving the breaking of two C=C bonds to form two new C=C bonds resulting in a pair of pentagons and a pair of heptagons (Figure 2.17). The dash lines indicate the rearrangement of the C=C bonds to reform hexagons.

![Stone–Wales transformation](image)

**Figure 2.17.** Stone–Wales transformation.

This temporary plastic deformation of the hexagonal lattice allows CNTs to sustain extreme strain with no signs of brittleness and plasticity. Hence, CNTs can bend, twist, kink, flattened and finally buckle under great axial compressive force and return to its
original state without fracturing.\textsuperscript{68} Their fracture strains range between 10\% and 30\%, which is better than most carbon fibers, which have values of 0.1\% to 2\% and can reversible be bent at angles in excess of 110\textdegree.\textsuperscript{69} Figure 2.18 shows a transmission electron microscope micrograph of a buckling MWNT.

![Figure 2.18. TEM micrograph and computer simulation of nanotube buckling.\textsuperscript{69}](image)

The ability of CNTs to conduct electricity is caused by each of its constituting sp\textsuperscript{2} hybridized carbon atom, having one free delocalized \pi electron, which can move freely around the structure. Since the flow of electrons is a current, CNTs can carry a charge and give rise to electrical conductivity (transfer energy). This conductivity is at its
maximum parallel to or along the tube axis and very low in a perpendicular (radial) direction. In a radial direction the electrons are confined by the one atom thick cylindrical sidewalls. In addition, the mobile π electrons flowing through CNTs obey the laws of quantum mechanics, functioning like a wave instead of a particle. In metals the flow of electrons encounters resistance as they collide into metal atoms and other electrons. The collisions result in the scattering of electrons, dissipation of energy and consequently a reduction in conductivity. The wave-like behavior of π electrons in CNTs allows them to flow unhindered by collision with the carbon atoms resulting in zero resistance along the tube. This quantum movement of an electron within nanotubes is called ballistic (no scattering) transport or conduction. This unique electronic character enables CNTs to carry a high current with little heating and low energy dissipation, which grants them a greater conductivity than metals. A metallic nanotube can carry electrical current density (carrying capacity) of $4 \times 10^9$ A/cm$^2$ which is 1000 times greater than that for copper wires before failing as a result of electromigration (self-electrolysis). Room temperature conductivity measurements have determined metallic SWNTs to have a conductivity of $10^5$ to $10^6$ Siemens per meter (S/m) and 10 S/m for a semiconducting SWNTs. The electrical conductivity of SWNTs is close to the in-plane conductivity of graphite, which is about $10^6$ S/m. The electrical conductivity of MWNTs is complicated to determine since each of the nanotubes can have different chirality, therefore different electronic character. However, studies have shown that the electrical conductivity of MWNTs is depended on the chirality of the outermost tube. Ebbesen et al. reported that the conductivity of a metallic outer nanotube of MWNTs to be in the range of $10^7$ to $10^8$ S/m ($10^5$ – $10^6$ S/cm).
The advanced thermal conductivity and thermal stability of CNTs are provided by the sigma sp² bonds, one the strongest covalent bonds in nature. Heat is transmitted throughout the CNT by the high frequency vibrations of the covalent bonds binding the carbon atoms together which through their atomic motion helps conduct heat through the hexagonal lattice. This differs from metals’ conduction of heat via non-ballistic electron transport. Like their electron conductivity, the thermal conductivities of CNTs exhibit high anisotropy. They are excellent thermal conductors over the length of the tube parallel to its axis, but insulating in the perpendicular or lateral direction. The room temperature axial thermal conductivity for MWNTs was measured to be 3,300 watts per kelvin per meter (W/K·m) and 3,500 W/K·m for SWNTs. These values are far exceeds the thermal conductivity of copper (385 W/K-m) and is significantly higher than that of diamond (1,000 – 2,200 W/K·m) one the best thermal conductors in existence. Their remarkable thermal stability allows CNTs to sustain temperatures of 750°C at atmospheric pressure and 2,800°C in a vacuum without thermal degeneration. They have demonstrated superconductivity below 20 K CNTs, thus they are being considered to be as room temperature superconductors.

In addition to their superior mechanical electrical and thermal properties CNTs also display magnetic anisotropy, have a large aspect ratio and surface area, and low density. Suspensions of CNTs aligned parallel to an applied magnetic field under SEM observation; displaying magnetic anisotropy with a maximum in the axial direction or parallel to the tube and a low in the radial direction. CNTs’ inherently enormous high
surface area is due to their nanoscale size and more importantly each carbon atom of individual CNTs has two surfaces, the inside and outside of the nanotube. Brunauer-Emmet-Teller measurements on purified CNTs yield a surface area of 1600 m$^2$/g, which is about 500 times more surface area per gram than other carbon fillers. Being only nanometers in diameter but able to attain lengths thousands of times greater, CNTs have a large aspect ratio (length divide by diameter) of 1000, the highest amongst any material available. This means that a very low loading (concentration) of CNTs is needed to form a percolation mixture to impart electrical conductivity to polymers compare to other nanofillers with lower aspect ratio such as carbon and stainless steel fibers. The electrical percolation threshold is the critical filler concentration at which a conversion from nonconductive to conductive state occurs. Furthermore, CNTs are light weight with a low density ($\rho$) ($\rho_{SWNT} = 0.6$ g/cm$^3$; $\rho_{MWNT} = 1–2$ g/cm$^3$) which makes them the ultimate nanofillers in composite materials.

2.5.3 Applications

Continuous research is dedicated to harnessing the exceptional properties of CNTs for practical applications in a number of diverse fields and disciplines where technologies are rapidly increasing, mainly nanotechnology, biomedical, engineering, material science, energy management. These explorative researches focus on taking advantage of the CNTs high aspect ratio, excellent thermal and electrical conductivity and its mechanical properties. Main areas were potential applications of CNTs are being developed include:
1. **Electrochemistry:** Potential electrochemical applications of CNTs are centered on increasing the energy capacity and the cycle time and decreasing the charging time of energy storage devices, and the environmentally friendly production of energy. It was observed that intercalating CNTs into electrodes of a lithium ion battery\textsuperscript{85-87} increased the battery’s energy capacity, electrical connectivity and mechanical integrity, leading to a longer cycle life. For the production of clean and renewable energy from mobile power sources, the use of CNTs as a microelectrode or support for the expensive transition metal platinum (Pt) catalysts in fuels cells, is not only cost efficient by reducing Pt usage by 60\%\textsuperscript{88} but leads to higher catalytic activity.\textsuperscript{8}

2. **Microelectronic Components and Devices:** Individual CNTs functioning as nanowires demonstrate exceptional performance by conducting high current densities of $1 \times 10^9$ to $1 \times 10^{10}$ A cm$^{-2}$ at temperatures of 250$^\circ$C. As ultimate field emitters, CNTs can serve as an electron gun used in flat panel displays and probes for scanning electron microscopes and atomic force microscopes.
3. **Nanofillers for Structural Composites**: Light weight high performance composites with multifunctional features have been made by incorporating CNTs into polymer, metallic and ceramic matrices for structural reinforcement, and improving or imparting electrical and thermal conductivity. CNTs as nanofillers have a distinct advantage over conventional fillers in having an extremely low loading content, less than 5 wt.% of the matrix’s mass, is required to bringing about a dramatic improvement in their hosts. This is very beneficial when weight is a concern.

2.6 Polymer/Carbon Nanotube Nanocomposites

The largest exploitation of CNTs as a nanofiller is focused on developing PCN. PCN combines the exceptional properties of CNTs with the diverse material characteristics (mechanical flexibility, biocompatibility, easy processibility, optical transparency, etc.) of polymers. The first PCN was created in 1994 by Ayajan et al. Since then PNCs have been fabricated from various classes of polymer matrices, such as thermosetting epoxies, thermoplastics, gels, elastomers, and conductive polymers in order to expand their spectrum of applications. CNTs in polymer matrices can convert an insulating polymer to a conductive composite and increase their tensile modulus and strength without sacrificing their existing properties and easy processibility. This makes recycling PCN a possibility as the CNT will not break down during the
subsequent processing. Additionally, CNTs can enhance the polymer’s thermal and oxidative stability and can serve as a highly effective flame retardant additive. These properties make PCN valuable in a wide variety of fields including land and air transport, space exploration, medicine and infrastructure.

CNTs may be the perfect nanofillers for polymer composites, however, their potential use as such strongly dependents on the dispersion of their agglomerates. Agglomeration of CNTs reduces their surface area hindering their interaction with the polymer host. A strong interfacial interaction is necessary for a successful transfer of the Thus, it is imperative not only to uniformly disperse the CNTs within the polymer matrix, but to stabilize the dispersion preventing re-aggregation of the CNTs. Also, whatever method of dispersion used, it must not damage the CNT structure, because it will significantly diminish their superior properties.

CNT agglomerates are dispersed by physical (energetic) agitation methods such as sonication, mechanical or magnetic stirring, shear mixing, extrusion, and ball milling. The first three methods require suspending the CNTs in an appropriate solvent that can interact with the CNTs facilitating their disaggregation. Amides, specifically N,N-dimethylformamide (DMF) and N-methylpyrrolidone are the most effective for the CNTs dispersion, because of their high polarity and free electron pair on the nitrogen atom, which interacts with the π-π conjugated system of CNTs. Sonication is the most employed method of dispersion, and can be used in two forms, high powered ultra-sonication using a horn or tip and mild sonication in a water bath. The latter technique at low power and short sonicating times is preferred, because it results in
minimal structure damage to the CNT. Regardless of the direct dispersion method, the
dispersion quality is unsatisfactory and none are effective in stabilizing the CNTs against
re-aggregation in solvents for extended periods.

Chemical functionalization of the sidewalls of the CNTs can significantly
improve their dispersion stability. Hybridized sp$^3$ carbons and carbons located at the
Stone-Wales defects and at vacancies in the CNT lattice are more reactive than the
majority sp$^2$ carbons. The sp$^3$ carbons along those located at the defects sites created by
the functionalization procedure can undergo addition reactions, thereby allowing the
covalent attachment of reactive chemical reagents. This method is referred to as defect
group functionalization of CNTs. Carboxyl and hydroxyl functional groups are
covalently attached to the CNTs sidewall by refluxing or sonicating pristine CNTs in
nitric and/or sulfuric acids or other oxidizing agents. The electrostatic repulsion
between polar functional groups on different CNTs and their attraction to the solvent
stabilized and prevents the re-aggregation of the dispersed CNTs in polar solvents.
However, acid oxidation and other chemical functionalization methods can cause
fragmenting and unzipping of the CNTs. This drastically reduces CNTs aspect ratio,
causing a degradation of its properties, poor CNT–polymer interfacial interaction and
limited transfer of CNTs properties to the polymer matrix. It is still an ongoing
investigation to find a low cost nondestructively method that efficiently disperses CNTs
into individual nanotubes.
A successful stable homogeneous dispersion of CNTs in polymer matrices without compromising the CNTs attractive properties will pave the way for preparing CNT-based polymer composites. Several preparation methods used for incorporating CNT into polymer matrices include solution casting\textsuperscript{110-112}, melt mixing\textsuperscript{113-115}, solution blending also known as coagulation precipitation,\textsuperscript{110, 111, 116} in situ polymerization of the monomer in the presence of CNTs\textsuperscript{117,118} and mechano-chemical pulverization (pan milling or twin screw pulverization).\textsuperscript{119}

Amongst these methods solution blending is the most used because of its simplicity, efficiency and ability to operate with small and large sample sizes. More importantly, this method can prepare PCNs from thermoplastic, thermosetting, elastomeric and thermoplastic elastomer matrices as long as the polymer is soluble in a solvent. Solution bending involves the dispersion of pristine or functionalized CNTs in a solvent used to dissolve the polymer by sonication or mechanical mixing. The CNT suspension is then mixed with a solution of the desired polymer at room or elevated temperatures with further agitation to distribute the CNTs. The viscosity of the polymeric solution should be very low to ensure the polymer chains can better infiltrate the CNTs agglomerates facilitating their disaggregation and distribution. Finally, the composite is recovered by precipitation of the CNTs/polymer suspension in a non-solvent for the polymer\textsuperscript{120} or by controlled evaporation of the solvent by drop\textsuperscript{121} or spin casting\textsuperscript{122} to form a composite film. Precipitation is the best recovery method because it instantaneously entraps the CNTs within polymer matrix while they are homogeneously dispersed and does not allow a chance for CNTs to form agglomerates. The CNTs are
non-covalently bonded to the polymer chains through hydrophobic interactions or through $\pi - \pi$ stacking provided the polymer has conjugated bonds, an aromatic substituent or heteroatoms with nonbonding electron pairs. The noncovalent interactions preserve the structural homogeneity of $\pi - \pi$ conjugation network of the CNTs sidewalls and therefore its mechanical, thermal and electrical properties.
CHAPTER III
EXPERIMENTAL

3.1 Purification of Chemical Reagents.

All glassware (reaction vessels and syringes) were meticulously clean in a base bath followed by drying in an oven at 100°C. All polymerization and hydrosilylation reactions were conducted under an inert nitrogen atmosphere in a dry box or by purging the reaction vessel. High purity nitrogen gas was further dried by flowing through a gas filter column filled with molecular sieves and drierite an active drying and moisture absorbing agent.

The utilization of pure reagents and solvents is vital for the synthesis of targeted molecular weights of PS and PDMS and their subsequent coupling via hydrosilylation to form the PS–b–PDMS–b–PS triblock copolymers. The following chemicals were used as received without any further purification: potassium hydroxide, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex in xylene (Karstedt Catalyst), sodium metal, ACS grade methanol, Benzophenone (BP), 99%, deuterated chloroform (d-CHCl₃), methylene chloride, acetic acid, anhydrous magnesium sulfate, acetone, 15% n–butyllithium (n–BuLi) in hexane, N,N-dimethylformamide (DMF), and single walled
carbon nanotubes with a (7, 6) chirality and 0.1 – 1.3 nm diameter. The carbon nanotubes are composed of > 90% carbon with 70% existing as SWNTs. The chemicals that were purified before use were styrene, toluene, benzene, 2,2,4,4,6,6,8,8-octamethyl-1,3,5,7-cyclotetrasiloxane (D₄), 1,2-divinyl-1,1,3,3-tetramethyldisiloxane (V₃M₄S₂). Their methods of purification are described below in detail.

3.1.1. Monomers: Styrene and Octamethylcyclotetrasiloxane

Monomers styrene and D₄ were purified by stirring over calcium hydride powder under nitrogen gas for 24 hours in order to remove any water present that can contaminate or cause unwanted termination of the extremely moisture sensitive anionic polymerizations. Using a short path distillation head apparatus, both monomers were collected via vacuum distillation prior to use directly into a round bottom flasks fitted with a stopcock adapter. The flask was sequentially purged with nitrogen gas.

3.1.2. Solvents

Benzene and tetrahydrofuran (THF) were refluxed over sodium metal with a small amount of benzophenone as an indicator of dryness, which formed the dark purple sodium benzophenone ketyl. The sodium metal was finely cut into small cubes to increase its surface area for more effective removal of traces quantities of moisture. The dried solvents were distilled immediately prior to use directly into the reaction flask. Toluene (b.pt. 110°C) was dried over calcium hydride overnight and collected by vacuum distillation. The dried toluene was stored over 3Å molecular sieves under an inert
atmosphere of nitrogen gas. Before use the dried toluene was filtered through a 0.45μm polytetrafluoroethylene (PTFE) syringe filter with a pore size of 0.45μm in the reaction flask fitted with a stopcock adapter and subsequently purged with nitrogen gas.

3.2. Methods of Synthesis

3.2.1. Living Anionic Polymerization of Styrene

The following section describes the experimental procedures used to synthesize PS of the target molecular weights of 2,000 (2K), 6,000 (6K) and 10,000 (10K) and its subsequent functionalization with the functional group chlorodimethylsilane (CDMS). To avoid environmental contamination the experimental procedure was carried out in a dry-box and is described as follows. Fifty milliliters (50 mL) of dried benzene was vacuum distilled directly into a 100 mL round bottom flask containing a teflon coated magnetic stir bar and fitted with a 10 mL stopcock adapter. The ratio of monomer to solvent was typically 1:10 (Styrene:Benzene) by volume. The reaction flask and a round bottom flask fitted with a rubber septum containing the styrene monomer were purged with nitrogen gas before being placed along with stainless steel needles, glass syringes, and the initiator n–BuLi, into a dry-box. The dry box was subsequently purged with nitrogen gas to create an inert atmosphere. Five (5 mL) of styrene followed by the calculated amount of n–BuLi were injected into the reaction flask using a glass syringe fitted with a stainless steel needle. After addition of the initiator the reacting mixture turn a reddish orange, characteristic of the living styryllithium anion. While inside the dry-box all stockcock adapters of the reacting flask was close and fitted with a rubber septum. A nitrogen filled
balloon attached to a syringe fitted with a needle was injected through the septum to maintain a positive pressure of inert atmosphere inside the reaction flask. The polymerization reaction was carried out at room temperature for 24 hours with continuous stirring. Termination of the polymerization was achieved by adding CDMS to the reaction flask. The reacting mixture turned colorless as the stryrl anion was terminated. The final polymer was pipetted slowly into stirring cold methanol and the resulting precipitate was vacuum filtered and then freeze dried on a Schlenk line to removal any residual solvents.

3.2.2. Anionic Ring Opening Polymerization of Octamethylcyclotetrasiloxane

Divinyl-terminated PDMS (v-PDMS) with targeted molecular weight values of 2K, 6K, and 10K g/mol were prepared by AROP of D₄ in the presence of V₂M₄S₂ as the endblocker. V₂M₄S₂ had a dual purpose of controlling the molecular weight of the polymer and functionalizing the PDMS for hydrosilylation coupling reaction. Bulk (no solvent required) polymerization of D₄ was initiated with potassium hydroxide (KOH) at 120°C. The high temperature was required because KOH is only soluble in D₄ at temperatures above 110°C and to evaporated water, a by-product formed from the reaction. KOH, finely grounded to facilitate its dissolution in D₄, was placed along with 30mL of D₄ and a determined amount of the V₂M₄S₂ in a 2-neck round bottom flask. One neck was fitted with a short path distillation head and the other was fitted a rubber septum for inserting a needle. Nitrogen gas was bubble through the solution via needle submerged below the surface of the solution to aid in the removal of water formed during
the polymerization. After three hours the reaction was stopped and allowed to cool to room temperature before 2M of acetic acid was added to the flask to neutralize the KOH. The resulting polymer and cyclic siloxane mixture was dissolved in methylene chloride (CH₂Cl₂) and then transferred to a separatory funnel. The mixture was washed three times with distilled water (d-H₂O) to remove the salt, potassium acetate and then dried over anhydrous magnesium sulfate (MgSO₄). MgSO₄ was removed by gravity filtration and PDMS was collected by rotatory evaporation. v-PDMS was devolatilized to remove the cyclic siloxanes formed during polymerization.

3.2.3. Hydrosilylation Coupling Reaction

Catalytic hydrosilylation was used to covalently couple different of molecular weights combinations of the silane functionalized PS (PS–SiH) and the v-PDMS prepolymer to form nine different molecular weight combinations of the PS–PDMS triblock copolymer listed in Table 3.1.
Table 3.1. The nine PS-\textit{b}-PDMS-\textit{b}-PS copolymers prepare from coupling different molecular weights of the PS and PDMS.

<table>
<thead>
<tr>
<th>Mn of PDMS</th>
<th>Mn of PS</th>
<th>No.</th>
<th>PS-\textit{b}-PDMS-\textit{b}-PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>2K – PDMS</td>
<td>2K - PS</td>
<td>I</td>
<td>2KPS-\textit{b}-2KPDMS-\textit{b}-2KPS</td>
</tr>
<tr>
<td></td>
<td>6K - PS</td>
<td>II</td>
<td>6KPS-\textit{b}-2KPDMS-\textit{b}-6KPS</td>
</tr>
<tr>
<td></td>
<td>10K - PS</td>
<td>III</td>
<td>10KPS-\textit{b}-2KPDMS-\textit{b}-10KPS</td>
</tr>
<tr>
<td>6K - PS</td>
<td>2K - PS</td>
<td>IV</td>
<td>2KPS-6KPDMS-2KPS</td>
</tr>
<tr>
<td></td>
<td>6K - PS</td>
<td>V</td>
<td>6KPS-6KPDMS-6KPS</td>
</tr>
<tr>
<td></td>
<td>10K - PS</td>
<td>VI</td>
<td>10KPS-6KPDMS-10KPS</td>
</tr>
<tr>
<td>10K - PS</td>
<td>2K - PS</td>
<td>VII</td>
<td>2KPS-10KPDMS-2KPS</td>
</tr>
<tr>
<td></td>
<td>6K - PS</td>
<td>VIII</td>
<td>6KPS-10KPDMS-6KPS</td>
</tr>
<tr>
<td></td>
<td>10K - PS</td>
<td>IX</td>
<td>10KPS-10KPDMS-10KPS</td>
</tr>
</tbody>
</table>

The hydrosilylation coupling reaction was carried out as follows. Working in a dry box under an inert atmosphere of nitrogen gas, PS-SiH and \textit{v}-PDMS prepolymers in a 1:2 molar ratio, along with a magnetic stirrer bar, 40 mL of dried toluene and two (2) drops of Karstedts catalyst were placed in a round bottom flask. The flask was fitted with a reflux condenser attached to drying tube filled dendrite and molecular sieves. The solution was refluxed for 4 days at a temperature between 65–70\degree C. Afterwards the PS-\textit{b}-PDMS-\textit{b}-PS triblock copolymers were collected via precipitation with methanol while rapid stirring, followed by vacuum filtration. It was then dried in a vacuum oven at room temperature.
3.2.4. Oxidation of SWNTs

SWNTs were oxidized by nitric acid following a procedure developed by Tchoul et al.\textsuperscript{123} A 50 mL centrifuge tube containing 20 mg of SWNTs and 40mL of DMF was sonicated in a water bath for 20 minutes at 50\textdegree{}C with a Brasonic Ultrasonic Cleaner. The suspension was then centrifuged and the supernate was removed via pipette. The SWNTs were washed with methanol followed by d-H\textsubscript{2}O before being dispersed in 20 mL of 8M nitric acid and sonicated for one hour. The carboxylic oxidized SWNTs were then washed with water followed by methanol and then DMF. The SWNTs were dispersed a second time in DMF and sonicated for one hour. The oxidized SWNTs were collected by vacuum filtration using a 47 mm diameter polytetrafluoroethylene filter paper with a pore size of 0.45\textmu{}m and a fritted funnel.

3.2.5. Preparation of PS-\textit{b}-PDMS-\textit{b}-PS/SWNTs Nanocomposites

The PS-\textit{b}-PDMS-\textit{b}-PS/SWNT nanocomposites were prepared by the following procedure described by Tchoul et al.\textsuperscript{123} A polymer solution prepared by dissolving 0.2 g (200 mg) of each of the nine PS-\textit{b}-PDMS-\textit{b}-PS triblock copolymers in 20 mL of DMF was stirred for 24 hours and then sonicated for 1 hour. Based on the mass of PS-\textit{b}-PDMS-\textit{b}-PS, 1wt. \% of oxidized SWNTs were dispersed in 10 mL of DMF, sonicated for 1 hour and then added to the polymer solution. Each mixture was stirred for 1 hour, sonicated for 1 hour and then stirred overnight. The mixtures were precipitated in rapidly stirring cold methanol, filtered with a PTFE filter and fritted funnel and then dried in a vacuum oven at 40\textdegree{}C.
3.3. Characterization

3.3.1. Nuclear Magnetic Resonance Spectroscopy

Proton ($^1$H) Nuclear Magnetic Resonance (NMR) analysis of PS and PDMS was performed on a Bruker Ultrashield-500 MHz NMR spectrometer to verify their termination by their respective functional end group and to estimate their number average molecular weight ($M_n$) values by end group analysis. All NMR samples were prepared in 5 mm borosilicate NMR tubes with approximately 40 mg of the copolymer dissolved in 1.0 mL of deuterated chloroform (CDCl$_3$). The $^1$H NMR spectra were referenced to the residual proton impurities in the CDCl$_3$ at δ7.26.

3.3.2. Fourier Transform Infrared Spectroscopy

A Perkin-Elmer Spectrum 65 Fourier Transform Infrared (FT-IR) spectrometer was used to verify the silane and divinyl functionalization of PS and PDMS respectively and the oxidation of SWNTs. All polymer and SWNTs samples were prepared by using the potassium bromide (KBr) pellet method.

3.3.3. Raman Spectroscopy

The Raman Spectra of pristine and oxidized SWNTs were recorded with a Bruker Infinity 1 Santerra spectrometer using a multiple laser source at 633 nm wavelength to determine the degree oxidation by estimating the intensity of the D-band ($I_D$) relative to the intensity of the G-band ($I_G$).$^{124}$
3.3.4. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) imaging of the PS-\(b\)-PDMS-\(b\)-PS triblock copolymer micellar aggregates was performed using a Keysight Technologies 8500 Field Emission SEM. Samples were prepared by dissolving 1 mg of the triblock copolymers in 1 mL of acetone and drop casting onto silicon wafers that were pre-washed with acetone. Since acetone is a good solvent for low molecular weight PS but a precipitant for PDMS, the PS-\(b\)-PDMS-\(b\)-PS triblock copolymers should form micellar aggregates with PS forming the corona and PDMS its core.

3.3.5. Dynamic Light Scattering

Dynamic Light Scattering (DLS) was used to measure the variation in the radius of the micellar aggregates formed by PS-\(b\)-PDMS-\(b\)-PS triblock copolymers composed of different molecular weight combinations of PS and PDMS homopolymers. The DLS measurements were performed on a Wyatt Technology DynaPro Nanostar instrument at ambient temperature. Samples were prepared by dissolving 1 mg of the triblock copolymers in 1 mL of acetone, filtered using a Millipore syringe filter with a pore size of 0.45 \(\mu\)m. The resulting polymer solution was stirred for 24 hours and then filtered directly into the cuvette for analysis.

3.3.6. Differential Scanning Calorimetry

The melting (\(T_m\)) and glass transition (\(T_g\)) temperatures of the neat PS-\(b\)-PDMS-\(b\)-PS copolymer and the PS-\(b\)-PDMS-\(b\)-PS/SWNT composites were investigated by
differential scanning calorimetry (DSC) using a TA Instrument Q 2000 differential scanning calorimeter, operating under nitrogen flow. The samples (ca. 7–10 mg) were weighed and sealed in Tzero hermetic aluminum sample pans. The samples were run using a heating rate and cooling rate of 5°C per minute from -80°C to 350°C for both the PS-b-PDMS-b-PS triblock copolymers and the PS-b-PDMS-b-PS/SWNT nanocomposites. The T\textsubscript{g} values were taken as the midpoint temperatures of the change in slope of the DSC curves while the T\textsubscript{m} values were taken as the peak minimum in the calorimetric curves.

3.3.7. Four Point Probe Electrical Resistivity Measurement

Electrical resistivity measurements of a batch of electrospun fibers and a single fiber of the PS-b-PDMS-b-PS/SWNT nanocomposites were performed using the four probe technique to obtain their current (I)-voltage (V) characteristic curves (I-V curve). I-V curves of an electrical device or component are a set of graphical curves, which are used to define its operation within an electrical circuit by showing the relationship between the current flowing through a device and the applied voltage across its terminals. The I-V characteristic curves for CNTs, shown in Figure 3.1., can show linear or nonlinear behavior, which respectively indicates the CNTs are behaving as an ohmic conductor or semiconductor.
Figure 3.1. The Current-voltage characteristic curves showing the electrical behavior of a metallic (conducting) and semiconducting CNT.

Fibers were electrospun from a 20% solution of PS-\textit{b}-PDMS-\textit{b}-PS/SWNT nanocomposite (compose of PS and PDMS with Mn =10,000) dissolved in DMF, when 20 Kilovolts were applied. They were collected on a silicon wafer 6 cm away from the syringe. A single strand of fiber was separated and placed on a conducting grid (Figure 3.2).

Figure 3.2. Electrical conducting grid.
The electrical resistivity measurements were taken by placing four probes, equal distance apart, in contact with the batch of fibers (Figure 3.3).

Figure 3.3 Four point probe set up.

A varying current is passed through the outer probes and induces a voltage in the inner voltage probes which was measured by a Keithley 6430 Sub-Femtoamp Remote Meter.
CHAPTER IV
RESULTS AND DISCUSSION

4.1 Introduction

The silane functionalized PS and vinyl terminated PDMS, as well as their coupling via catalytic hydrosilylation to formed nine PS-\textit{b}-PDMS-\textit{b}-PS triblock copolymers were characterized by FT – IR and \textsuperscript{1}H NMR spectroscopy. DSC thermal analysis of the PS-\textit{b}-PDMS-\textit{b}-PS/SWNTs nanocomposites was employed to determine if SWNTs will selectively interact with the PS and PDMS block of the triblock copolymer. It was expected that SWNTs will interact with both polymer blocks through hydrophobic van der Waals interactions. However, factors such as the tacticity, molecular weight and the physiochemical properties of the individual homopolymers may cause the SWNTs to have a higher affinity for one of the constituting blocks.

4.2 Synthesis of ω-Silyl Hydride Functionalized Polystyrene

\textsuperscript{1}H NMR and FT-IR spectroscopic analysis was used to verify termination of the macrostyryllithium anion with CDMS. Figure 4.1 shows the \textsuperscript{1}H NMR spectrum obtained for PS produced by LAP.
The aryl protons from the phenyl ring substituents gives the most intense peaks around 6 - 8 ppm followed by the alkyl protons of the backbone ranging from 1.5 – 2.5 ppm. The protons introduced from the n–BuLi initiator were observed at 0.8 – 1.3 ppm. More importantly, the $^1$H NMR spectrum shows the characteristic peak for the silane proton ca. 3.8 ppm. The intensity of silyl hydride peak was weak but distinct, and indicates the successful silyl functionalization of the PS chains. FT-IR spectroscopic analysis provided further confirmation for the incorporation of silyl hydride functionality at the terminal
polystyrene chain end. An absorption band corresponding to a Si–H bond stretching vibration was observed around 2115 cm\(^{-1}\) along with CH\(_3\) deformation and CH\(_3\) rocking absorptions at 1250 cm\(^{-1}\) and 890 cm\(^{-1}\) respectively (Figure 4.2). The peak located 3400 cm\(^{-1}\) is due to water absorbed by the hygroscopic KBr.

![FT-IR spectrum of silyl hydride functionalized polystyrene.](image)

The M\(_n\) of the PS chains was quantitatively calculated by \(^1\)H NMR end group analysis using the protons of the butyl and silane groups. Table 4.1 shows target M\(_n\) and the calculated M\(_n\) as well as the percentage yield of each polymer.
Table 4.1. Comparison of the target and calculated $M_n$ for polystyrene.

<table>
<thead>
<tr>
<th>Target $M_n$</th>
<th>Calculated $M_n$</th>
<th>Percentage Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,000</td>
<td>3,060</td>
<td>90%</td>
</tr>
<tr>
<td>6,000</td>
<td>5,436</td>
<td>81%</td>
</tr>
<tr>
<td>10,000</td>
<td>10,426</td>
<td>85%</td>
</tr>
</tbody>
</table>

4.3. Synthesis of $\alpha,\omega$-Divinyl Functionalized Polydimethylsiloxane

PDMS of target molecular weights of 2K, 6K and 10K were prepared by bulk AROP catalyzed by potassium hydroxide in the presence of the endblocker $V_2M_4S_2$. The $^1H$ NMR spectrum, shown in Figure 4.3 was dominated by the intense peak of the methyl protons of the Si-CH$_3$ group ranging from -0.1 to 0.1 ppm. Also, ranging from 5.8 to 6.2 ppm, the spectrum reveals three doublets of doublets resonance splitting pattern, which corresponds to the three vinylic end group protons.
Figure 4.3. $^1$H NMR of $\alpha,\omega$-divinyl functionalized PDMS

The protons of the terminal vinyl group were used to determine the $M_n$ of the PDMS by $^1$H NMR end group analysis. The target $M_n$ and $M_n$ estimated by $^1$H NMR end group analysis are listed in table 4.2 along with the polymer percentage yield.
Table 4.2. Comparison of the target and calculated $M_n$ for polydimethylsiloxane.

<table>
<thead>
<tr>
<th>Target Mn</th>
<th>Calculated Mn</th>
<th>Percentage Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,000</td>
<td>1,715</td>
<td>93</td>
</tr>
<tr>
<td>6,000</td>
<td>5,390</td>
<td>90</td>
</tr>
<tr>
<td>10,000</td>
<td>10,250</td>
<td>84</td>
</tr>
</tbody>
</table>

FT – IR spectroscopic analysis also verified the synthesis of divinyl functionalized PDMS. The FT – IR spectrum in Figure 4.4 shows a strong at 791 cm$^{-1}$ arising from the Si–CH$_3$ rocking transition. Several strong peaks ranging from 1000–1100 cm$^{-1}$ are observed due to the Si–O–Si antisymmetrical stretching. Most importantly, a small is seen a 1671 cm$^{-1}$ which corresponds to the C=C stretching band of the vinyl groups. This stretching band confirms the successful covalent bonding to or the termination of the PDMS chain with V$_2$M$_4$S$_2$ functional group.

Successful functionalizing the PS and PDMS with silane and V$_2$M$_4$S$_2$ moieties respectively allows for the two homopolymers to undergo a hydrosilylation coupling reaction to prepare the desire triblock copolymer PS-$b$-PDMS-$b$-PS.
4.4. Synthesis of PS-b-PDMS-b-PS Triblock Copolymer

The nine different molecular weight combinations of PS and PDMS (see table 3.1) were prepared by a catalytic hydrosilylation coupling reaction between the silyl hydride functional group of PS with the unsaturated vinyl bonds of PDMS. Figure 4.5 shows the comparative FT-IR spectra of 2K PS-SiH, 2K v-PDMS and their corresponding triblock copolymer.
A successful coupling of the homopolymers was confirmed by the disappearance of the stretching band of Si–H and C=C at 2111 cm\(^{-1}\) and 1640 cm\(^{-1}\) respectively. The latter has been replaced by the aromatic (ar) C=C stretching band of the PS phenyl rings.

The coupling of the PS and PDMS homopolymer was also confirmed by \(^1\)H NMR spectroscopy. The Si–H observed at 3.8 ppm in the \(^1\)H NMR spectrum of PS–SiH (Figure 4.6a) and C=C of the vinylic protons ranging from 5.8 to 6.2 ppm in the \(^1\)H NMR spectrum of v–PDMS (Figure 4.6b) was not observed in the \(^1\)H NMR spectrum of the PS-\(b\)-PDMS-\(b\)-PS triblock copolymer (Figure 4.6c).
Scanning electron microscopy also provided visual confirmation of the successful covalent coupling between the prepolymers. The covalent bonds between the immiscible constituting blocks of PS-\textit{b}-PDMS-\textit{b}-PS will cause the copolymer to self-assemble into micellar aggregates in acetone. The SEM micrographs presented in Figure 4.7 show that all of the nine PS-\textit{b}-PDMS-\textit{b}-PS triblock copolymers listed in Table 3.1 self-assemble into micellar aggregates of various hydrodynamic radii ($R_h$).
Figure 4.7. SEM micrographs obtain for all nine PS-b-PDMS-b-PS: (a) I, (b) II, (c) III, (d) IV, (e) V, (f) VI, (g) VII, (h)VIII, and (i) IX.
Acetone is a good solvent for low molecular weight PS but a poor solvent for PDMS. Therefore, the micellar aggregates will have a PS corona and the PDMS will form the core to limit its contact or interaction with the acetone solvent. The \( R_h \) of the micelles were measured by DLS and the results are listed in Table 4.3.

Table 4.3. Hydrodynamic radii of PS-\( b \)-PDMS-\( b \)-PS micellar aggregates.

<table>
<thead>
<tr>
<th>No.</th>
<th>Triblock Copolymers</th>
<th>Micelle Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>I</td>
<td>2KPS-2KPDMS-2KPS</td>
<td>1.9</td>
</tr>
<tr>
<td>II</td>
<td>6KPS-2KPDMS-6KPS</td>
<td>2.4</td>
</tr>
<tr>
<td>II</td>
<td>10KPS-2KPDMS-10KPS</td>
<td>2.9</td>
</tr>
<tr>
<td>IV</td>
<td>2KPS-6KPDMS-2KPS</td>
<td>2.1</td>
</tr>
<tr>
<td>V</td>
<td>6KPS-6KPDMS-6KPS</td>
<td>2.5</td>
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<tr>
<td>VI</td>
<td>10KPS-6KPDMS-10KPS</td>
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</tr>
<tr>
<td>VII</td>
<td>2KPS-10KPDMS-2KPS</td>
<td>2.4</td>
</tr>
<tr>
<td>VIII</td>
<td>6KPS-10KPDMS-6KPS</td>
<td>2.7</td>
</tr>
<tr>
<td>IX</td>
<td>10KPS-10KPDMS-10KPS</td>
<td>3.0</td>
</tr>
</tbody>
</table>

As expected the \( R_h \) of the triblock copolymers increased as the molecular weight of the PS and PDMS constituting blocks were increased.
4.5. Oxidation of SWNTs

Oxidation of the SWNTs was imperative to overcome van der Waals forces of attraction to prevent aggregation of the SWNTs and to achieve a uniform dispersion throughout the PS-b-PDMS-b-PS triblock copolymer matrix. This will allow the successful transfer of the SWNTs properties to triblock copolymer matrix. In Figure 4.8, the Raman spectrum of pristine SWNTs is compared to that of SWNTs after acid oxidation to confirm the oxidation of SWNTs.

Figure 4.8. Raman Spectrum of (a) pristine and (b) oxidized SWNTs.

(a) Pristine SWNTs

G*: 1595.1 cm\(^{-1}\); \(I_G\): 740.4
G*: 1555.2 cm\(^{-1}\); \(I_G\): 309.6
D: 1309.7 cm\(^{-1}\); \(I_D\): 68.2

(b) Oxidized SWNTs

G*: 1595.1 cm\(^{-1}\); \(I_G\): 2356.7
G*: 1555.2 cm\(^{-1}\); \(I_G\): 1104.4
D: 1309.7 cm\(^{-1}\); \(I_D\): 204.9
Two distinct vibrational bands were used to determine the degree of oxidation of the SWNTs. The first band is the disorder induced (D-) band, identified at 1309 cm\(^{-1}\). It originates from the presence of nanotube sidewall structural defects, such as carbonaceous impurities like amorphous carbon, sp\(^3\) hybridized carbon atoms and molecules linked to the nanotube sidewall via chemical functionalization.\(^{125}\) The second band, the tangential mode or graphitic (G–) band is associated with the collective tangential planar stretching vibration of the sp\(^2\) carbon atoms and is independent of structural disorder. It is split into a G\(^{+}\) and G\(^{-}\) components observed at 1595.05 cm\(^{-1}\) and 1553.11 cm\(^{-1}\) respectively. The most intense component, G\(^{+}\), and its lesser counterpart G\(^{-}\) correspond, respectively, with vibration of the carbon atoms along the nanotube axis and along the circumferential direction of the SWNTs.\(^{126,127}\) Both bands exhibit a Lorentzian line shape indicating the SWNTs were semiconducting and isolated.\(^{128}\) The ratio intensity of G– and D– bands \((I_D/I_G)\) has been used to evaluate the purity of SWNTs when carbonaceous impurities are present\(^{129-131}\) and to quantify their structural quality or defect density of CNTs when the impurities are absent or at low levels.\(^{124,132}\) Thus, \(I_D/I_G\) analysis can be used to obtain information regarding the amount of defects introduced upon treatment with nitric acid.\(^{133}\) However, the intensity of both G– (I\(_G\)) and D– bands (I\(_D\)) decreased after acid treatment. The reduction in the intensities can be explained by the disruption of the translational symmetry of the particularly highly symmetrical SWNTs due to oxidation.\(^{134}\) Consequently, resonance enhancement was lost as the SWNTs become more asymmetric leading to a decrease in band intensity. Nevertheless, the reduction in I\(_D\) and I\(_G\) indicates the successful oxidation of SWNTs.
FT–IR spectroscopy provided further proof supporting the oxidation of SWNTs. Figure 4.9 shows a comparative FT–IR data for the pristine SWNTs and nitric acid treated SWNTs.

![FT–IR Spectra](image.png)

Figure 4.9 FT–IR spectra of (a) pristine and (b) oxidized SWNTs.

For the pristine SWNTs no vibrational signal was observed (Figure 4b), however, after acid treatment three new peaks appear (Figure 4.9a). A broad peak identified at 3433 cm\(^{-1}\) is attributed to the characteristics stretching band of a hydroxyl functionality (-OH) in a
solid or concentrated alcohols. Peaks at 1625 cm\(^{-1}\) and 1383 cm\(^{-1}\) were assigned to a carbonyl (C=O) stretching and –OH in plane bending respectively. The presence of a hydroxyl and carbonyl confirms that carboxylic functionalities was attached to the surface of the SWNTs. The extensive conjugation of the SWNTs decreases the C=O bond strength shifting its vibrational peak frequency to lower wavenumbers from that which is common for carboxylic acid (1705-1720 cm\(^{-1}\)). Figure 4.9 shows the comparison of oxidized (left) and pristine (right) SWNTs dispersed in DMF in a sonication bath.

![Image](image.png)

Figure 4.10. The dispersion of oxidized SWNTs (left) and pristine SWNTs (right) in DMF 3 hours after sonication.

The oxidized SWNTs (SWNTs–COOH) remain effectively dispersed for over 3 hours due to charge repulsion between the carboxylic groups on individual SWNTs. The pristine SWNTs aggregated to the bottom of the vial within 30 minutes after removal from the sonication bath.
4.6. DSC Thermal Analysis of PS-\textit{b}-PDMS-\textit{b}-PS/SWNTs Nanocomposites.

Based on the mass of the triblock copolymers, 1wt. % of SWNTs-COOH was incorporated into the PS-\textit{b}-PDMS-\textit{b}-PS matrices via solution blending (coagulation precipitation. In general it was expected that SWNT interaction with both PS block and PDMS blocks will occur via hydrophobic van der Waals forces of attraction. The nonpolar SWNTs will interact with the equally nonpolar PS block and with the PDMS via nonpolar methyl substituents attached to the silicon atoms. For the PDMS block this interaction will occur with the flexible PDMS physically wrapping around the rigid SWNTs as illustrated in figure 4.11

![Illustration of the PDMS block noncovalently wrapping around the SWNTs.](image)

The stiff PS block interaction may occur by wrapping or simply being in close proximity to the SWNTs. Additional, interaction between PS and SWNTs will occur by $\pi - \pi$ interaction between the $\pi - \pi$ conjugated network of the SWNTs and the phenyl substituents of PS (Figure 4.12).
Figure 4.12. The $\pi - \pi$ interaction between the $\pi - \pi$ conjugated network of SWNTs and the phenyl substituents of PS.

The PS-$b$-PDMS-$b$-PS and SWNTs interactions may cause changes to occur in both the PS and PDMS transition temperatures. To determine whether SWNTs-COOH prefers to interact with the PS or PDMS block, DSC thermal analysis was used to monitor the changes in $T_g$ of PS and the $T_m$ of PDMS. The thermograms of each copolymer and its corresponding nanocomposite are arranged into three different groups in order to compare changes in their transitional temperatures. In each group the molecular weight of the PDMS middle block is held constant while that of the PS end blocks is varied. Table 4.4 shows the copolymers group assignment.
Table 4.4. The group assignment for the nine different molecular weight combinations of the PS-\textit{b}-PDMS-\textit{b}-PS triblock copolymers and their corresponding nanocomposites.

<table>
<thead>
<tr>
<th>Group</th>
<th>No.</th>
<th>PS-\textit{b}-PDMS-\textit{b}-PS) /Nanocomposites</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>I</td>
<td>2KPSt – 2KPDMS – 2KPSt</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>6KPSt – 2KPDMS – 6KPSt</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>10KPSt – 2KPDMS – 10KPSt</td>
</tr>
<tr>
<td>B</td>
<td>IV</td>
<td>2KPSt – 6KPDMS – 2KPSt</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>6KPSt – 6KPDMS – 6KPSt</td>
</tr>
<tr>
<td></td>
<td>VI</td>
<td>10KPSt – 6KPDMS – 10KPSt</td>
</tr>
<tr>
<td>C</td>
<td>VII</td>
<td>2KPSt – 10KPDMS – 2KPSt</td>
</tr>
<tr>
<td></td>
<td>VIII</td>
<td>6KPSt – 10KPDMS – 6KPSt</td>
</tr>
<tr>
<td></td>
<td>IX</td>
<td>10KPSt – 10KPDMS – 10KPSt</td>
</tr>
</tbody>
</table>

The DSC thermograms for the uncoupled homopolymers of PS and PDMS are shown in Figure 4.11. As expected the $T_g$s for PS and the $T_m$s for PDMS increased with increasing molecular weight. Both transition temperatures will reach an asymptotic limit at higher molecular weights. The $T_g$ (-127 to -125 °C) and cold crystallization temperature (-98 to -92 °C) of the PDMS middle block will not be observed in its DSC thermograms due to the operational limitations of the DSC instrument. However, a broad melting range ($T_m$) is observed at 47.46 – 38.32° C for the 6K and at 47.40 – 36.61° C for 10K PDMS homopolymer. The presence of a $T_m$ endotherm proves crystallization of PDMS occurs because melting is an endothermic process characteristic of crystalline or semi-crystalline materials. If an endotherm for melting is not shown in the PDMS thermograms it was not observed in the thermal analysis.
Figure 4.13. DSC thermograms for the homopolymers of (a) PS and (b) PDMS.

Group A

Figure 4.14 shows the DSC thermograms for the neat PS-\(b\)-PDMS-\(b\)-PS copolymers and PS-\(b\)-PDMS-\(b\)-PS / SWNTs-COOH composites assign to group A.
Figure 4.14. DSC thermograms for copolymers in group A and their nanocomposites.
Nanocomposite I (Figure 4.14) exhibits an increase in the $T_g$ for the PS block from 79.52°C to 84.96°C. The increase in $T_g$ is attributed to the SWNTs-COOH impeding the segmental mobility of the PS chains by interacting with the chains. This impedance results from the general observation that low molecular weight polymers do not disperse CNTs as effectively as high molecular weight polymers due to their small volume (occupied space). Within the confined small volume there is a greater chance of SWNTs-COOH hindering the PS chains mobility. Greater volume becomes available as the molecular weight of the PS blocks increases from 6K to 10K in nanocomposites II and III respectively. The less confined SWNTs will act as plasticizers and penetrate the spaces between the PS chains in the glass microdomains causing an increase in the distance or free volume between the PS chains. The greater distance weakens the $\pi - \pi$ interaction and van der Waals cohesive forces between the PS blocks. Less heat is now required to initiate segmental motion in the PS chains, thus lowering its $T_g$.

Surprisingly, the thermogram for nanocomposite II (Figure 4.12) also displays a melting endotherm for the 2K PDMS at -44.63°C, whereas for the uncoupled homopolymer of 2K PDMS (Figure 4.11b) a melting endotherm was not observed. This means the incorporated SWNTs-COOH is also interacting with PDMS block as nucleating agents accelerating its rate of crystallization. However, a melting endotherm for PDMS is not observed for nanocomposites I and III. This could be explained by the migration of the SWNTs-COOH to PS block as its molecular weight increases. In nanocomposite I the 2K PDMS block may be saturated with SWNTs. Since the SWNTs are in close proximity of each other they aggregate inhibiting their ability to function as
nucleating sites. As the molecular weight of PS increase to 6K in nanocomposite II some of the SWNTs-COOH can migrate there due to the greater availability of space. The remaining quantities of SWNTs in the PDMS block are probably at the optimal critical concentration (percolation threshold) for crystallization to occur. The migration of SWNTs-COOH will continue in nanocomposite III until the quantity of SWNTs-COOH in the PDMS block decreases below the percolation threshold for crystallization. It is hypothesized that the SWNTs migration from the PDMS block to the PS blocks only occurs because the 2K PDMS block is too small accommodate all the SWNTs. Within close proximity to each other electrostatic repulsion will compel the oxidized SWNTs to separate and move into the only available space provided by the PS blocks. This gives a first sign that the SWNTs may prefer to interact with the PDMS block.

**Group B**

Incorporating SWNTs-COOH into group B copolymers, where molecular weight of the PDMS block is 6K, has a completely reverse effect on the Tg of the PS blocks in comparison to their group A counterparts. Nanocomposites V and VI now show an increase in Tg of the PS block due to the segmental mobility of the PS blocks being hindered by the SWNTs, while copolymer IV shows a decrease due to the plasticization effect of the SWNTs. The DSC thermograms of group B copolymers and their nanocomposites are shown in Figure 4.15.
Figure 4.15. DSC thermograms for copolymers in group B and their nanocomposites.
SWNTs reverse effect on the \( T_g \)s of the PS blocks is another sign the SWNTs may prefer to interact with the PDMS block. The 6K PDMS block can accommodate all or the majority of the SWNTs, therefore very little SWNTs will migrate to the PS block even as its size increases to 6K and 10K in nanocomposites V and VI, respectively. Since the SWNTs content in the PS blocks of nanocomposites V and VI remains constant its wt. % will decrease in relation to the increasing molecular weights of the PS blocks. According to Sathyanarayana et. al. lower wt. % of CNTs results in an increase \( T_g \). This supports the DSC results as nanocomposite VI shows a greater increase in its \( T_g \) (82.96\(^\circ\)C to 95.34\(^\circ\)C) than nanocomposite V (79.08\(^\circ\)C to 82.47\(^\circ\)C). Nanocomposite IV has the greatest wt. % of SWNTs which may cause its \( T_g \) to decrease instead of increasing.

Interestingly, the thermogram for nanocomposite IV also shows two endothermic melting peaks at -56.91\(^\circ\)C (\( T_m1 \)) and at 43.91\(^\circ\)C (\( T_m2 \)), with a crystallization exotherm occurring between the two \( T_m \)s at 48.17\(^\circ\)C. This thermal behavior is exhibit only by high molecular weight cyclic siloxanes and linear PDMS, as well as other polymers when they are rapidly cooled below their \( T_g \). In literature three possibilities have been proposed to account for the two melting points. They are (i) the formation of crystallites of different sizes or less perfect crystallites, (ii) the melting – recrystallization of the original crystallites and their subsequent melting, and (iii) the formation of different crystallites. Since linear PDMS have only one crystal structure, a helix conformation in a monoclinic cell, the latter proposal could be dismiss as it was unconfirmed by experimental studies. However, these studies were based on rapidly cooling PDMS and not its crystallization induce by SWNTs. If SWNTs can
induce the formation of isomorphic crystals it can be confirmed by cryo-crystallography. For now the two melting endotherms of PDMS are attributed to the melting and recrystallization of small and/or imperfect or unstable crystallites to more order crystallites which represents the major endotherm at \( T_{m2} \).\(^{144, 150-152}\)

Although the nanocomposite was not cooled rapidly the SWNTs-COOH serving as nucleating sites increase crystallization which causes the double melting phenomenon. However, only a single \( T_m \) is observed for nanocomposite V and none is observed for copolymer VII. This can be explained by the physical crosslinks of the larger 6K and 10K PS blocks providing strong anchoring entanglements that suppress the rearrangement or reorganization of the 6K PDMS block to form crystals despite the nucleation effect of the SWNTs. The 6K PS segment provides just enough resistance to slow down, but does not prevents, the rearrangement of the PDMS segments into a crystal lattice. A slower formation of crystal leads to more perfect crystals, made evident by a single \( T_m \). The 10K PS of nanocomposite VI prevents crystallization completely due to the absence of a melting endotherm.

Group C

The DSC thermograms of VII and IX, shown Figure 4.16, provide further and more conclusive evidence the SWNTs-COOH has preference for the PDMS block.
Figure 4.16. DSC thermograms for copolymers in group C and their nanocomposites.
There is a negligible difference between the $T_g$ values for the PS block of the neat triblock copolymers and their nanocomposites. This means there must be either no or a very minute quantity of SWNTs interacting with PS phase in order for its $T_g$ to remain relatively unchanged. On the other hand SWNTs are confirmed to be interacting as a nucleating agent with the PDMS microphase, facilitating its crystallization, as indicated by the presence melting endotherms in both VII and IX. This is evident in nanocomposite VII by the appearance of the double melting endotherms where initially there was only a single melting endotherm, and in IX where initially in the neat copolymer a melting endotherm was not observed but is observed in the nanocomposite.

SWNTs-COOH preference for the PDMS segment in nanocomposites VI, IX and for those in group B is a feasible proposition, when one considers the ability of the homopolymers to disperse and interact with SWNTs-COOH. Atactic PS as well as other atactic polymers do not disperse nor interact with CNTs as effectively as isotactic and syndiotactic counterparts due to their irregular or random microstructure. Also, the difference in polarity between the non-polar PS blocks and the polar carboxylic group of oxidized SWNT has been reported to cause poor interactions with the polymer matrix. PDMS is the only known polymer to effectively disperse CNTs for extended time without complex dispersion methods or chemical functionalizing the sidewalls of CNTs. In addition, the difference in electronegativity between the silicon and oxygen atoms makes the siloxane backbone partially polarized. Thus, the polar carboxylic group of the oxidized SWNTs might be attracted to the polar PDMS backbone although its access might be blocked by the methyl substituents bonded to the silicon atom.
These observations suggest that SWNT may prefer the PDMS block in the copolymers depending on whether the PDMS domains are of sufficient dimensions.

4.7. Electrical Resistivity Measurement of the Nanocomposite IX

Nanocomposites VII and IX were selected to be electrospun into fibers to determine, if the SWNTs–COOH preference for the PDMS will affect the triblock copolymer’s electrical conductivity. Electrospinning of VII was unsuccessful possibly due to the high wt. % of the PDMS. PDMS homopolymer cannot be electrospun due to its very low glass transition temperature. A 20% solution of nanocomposite IX in DMF was successfully electrospun into fibers onto a silicon wafer 6 cm away from the syringe with an applied potential of 20 kilovolts. The I–V characteristic of a single fiber was studied to determine, if it possess ohmic (metallic) conductor or semiconductor characteristics or will be non-conducting. The I–V curve for nanocomposite IX is shown in Figure 4.17.
Figure 4.17. The I-V characteristic curve of a single fiber of nanocomposite IX.

The fiber of nanocomposite IX exhibits a non-ohmic or nonlinear characteristic curve, indicating it has semiconducting behavior. Raman spectroscopic analysis of the pristine and oxidized SWNTs shows the G-band of both has a Lorentzian line shape, indicating both are semiconductors. This means, the SWNTs preference for the PDMS block does not influence the conducting behavior of the nanocomposite since its semiconducting behavior corresponds to electrical semi-conductivity of the SWNTs.
CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

5.1. Conclusions

The DSC data suggests that SWNTs simultaneously interact with both the PS and PDMS blocks. SWNTs–PS interaction is inferred from the SWNTs ability to increase or decrease the $T_g$ of PS block. The increase in the $T_g$ of PS is most likely due to the SWNTs hindering the PS chain segmental mobility. A plasticization effect, where the SWNTs create more free volume between the PS chains, will cause the $T_g$ of PS to decrease. Within the PDMS block the SWNTs act as nucleation sites accelerating its crystallization. This is made evident by the appearance of melting endotherms in the thermograms of some of the nanocomposites. However, the data also suggest that SWNTs possess a higher affinity for the PDMS block. SWNTs will prefer to interact with the PDMS block, if the volume of the PDMS block can effectively disperse the SWNTs. Only when the PDMS block becomes saturated with SWNTs, will they migrate to and interact with the PS blocks. This indicates that despite the mutual hydrophobic interactions between the SWNTs and the polymer blocks other factors influence SWNTs preference for the PDMS. One such factor is the tacticity of PS. Syndiotactic and isotactic PS, due to their regular arrangement, interact and disperse CNTs more effectively than their randomly arranged atactic counterpart.
5.2. Recommendations

A research effort should be undertaken involving the preparation of the PS-\textit{b}-PDMS-\textit{b}-PS triblock copolymer with isotactic PS since it can disperse and interact with CNTs better than atactic PS. Uniform dispersion of the SWNTs through the entire triblock copolymer is imperative so the exceptional properties can be transferred to both polymer blocks. It is also recommended the DSC experiments should be conducted at lower temperatures to observe the effect of the SWNT on the T_g and cold crystallization temperature of PDMS. This will give a more direct indication of the interaction between SWNTs and the PDMS block than the T_m. Additional recommended areas of investigation include determining the critical SWNT content or percolation threshold for optimal electrical conductivity and evaluation of the rheological properties of the PS-\textit{b}-PDMS-\textit{b}-PS fiber.
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