Design and investigation of block copolymers for dispersion of carbon nanotubes in polymer matrices

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**NANYANG
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**DESIGN AND INVESTIGATION OF BLOCK
COPOLYMERS FOR DISPERSION OF CARBON
NANOTUBES IN POLYMER MATRICES**

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

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A thesis submitted to the Nanyang Technological University in
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List of Abbreviations

1-D	one-dimensional
2-D	two-dimensional
AFM	atomic force microscopy
AFDA	2,7-diamino-9,9'-dioctylfluorene
APA	4-aminophenethyl
ASO	4,4'-diaminodiphenyl sulfone
ATRP	atom transfer radical polymerization
BPDA	3, 3', 4, 4'-biphenyltetracarboxylic dianhydride
BPADA	2,2-Bis[4-(3,4-dicarboxyphoxy)phenyl]propane anhydride
CL	caprolactone
CNTs	carbon nanotubes
DCM	dichloromethane
DMAc	<i>N, N'</i> -dimethylacetamide
DMAP	4-(dimethylamino) pyridine
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DMSO- <i>d</i> ₆	deuterated dimethylsulfoxide
DSC	differential scanning calorimetry
EP	epoxy
FE-SEM	field-emission scanning electron microscopy
FT-IR	fourier transform infrared
GO	graphite oxide
GPC	gel permeation chromatography
HAB	3, 3'-dihydroxy-4, 4'-diaminobiphenyl
HOMO	highest occupied molecular orbital
IFSS	interfacial shear strength
LUMO	lowest unoccupied molecular orbital
MAC	2-methyl-2-(allyloxycarbonyl)propylene carbonate
<i>m</i> -CPBA	3-chloroperoxybenzoic acid
MWNTs	multi-walled carbon nanotubes
NaDDBS	dodecylbenzene sulfonate
NMR	nuclear magnetic resonance

ODA	oxydianiline
ODPA	4, 4'-oxydiphthalic anhydride
PA	polyamide
PAA	poly(amic acid)
PAAS	poly(amic acid) with sulfone groups
PBI	polybenzimidazole
PC	polycarbonate
PCL	polycaprolactone
PDI	polydispersity index
PE	polyester
PEEK	polyether-etherketone
PEO	poly(ethylene oxide)
PFO	poly(9,9-dioctylfluorenyl-2,7-diyl)
PFS	poly(pentafluorostyrene)
PI	polyimide
PI-BDA	polyimide- <i>graft</i> -bisphenol A diglyceryl acrylate
PI-GNE	polyimide- <i>graft</i> -glyceryl 4-nonylphenyl ether
PLA	polylactide
PMDA	pyromellitic dianhydride
PMMA	poly(methyl methacrylate)
PmPV	p-phenylenevinylene
PS	polystyrene
SDBS	sodium dodecylbenzenesulfonate
SDS	sodium dodecylsulfate
SWNTs	single-walled carbon nanotubes
TB	triblock copolymer
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
THF	Tetrahydrofuran
TPEs	thermoplastic elastomers
UV-vis-NIR	ultraviolet-visible-near infrared

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Abstract

Single-walled carbon nanotubes (SWNTs) are promising nanofillers for synthesizing lightweight, strong polymeric nanocomposites because of their large aspect ratios, low densities, and exceptional mechanical, electrical, and thermal properties. To fully utilize the remarkable properties of SWNTs to mechanically reinforce polymers, investigators' should focus on nanotube properties such as their content, dispersibility, matrix-interfacial adhesion, and alignment. This thesis focuses on the dispersion and functionalization of SWNTs for mechanical reinforcement of the polymer matrices polyimide (PI) and epoxy (EP).

In the first study, poly(amic acid) with sulfone groups complexed with chromium and carbon nanotubes (CNTs), labelled as PAAS-Cr-CNT, was synthesized and shown to be effective in increasing the interaction and interfacial bonding between poly(amic acid) and CNTs compared with traditional non-covalent functionalization, as evidenced by FE-SEM and mechanical testing. The modulus of the composite film increased by up to 35% with 2 wt% CNT loading, and its strength could still be maintained compared to the pure polyimide matrix. However, the dispersion of CNTs was not optimum because of the interaction of chromium with multiple SWNTs during the reaction.

To eliminate the interaction issue and further improve the dispersion of CNTs, a triblock copolymer system was introduced. Polycaprolactone-polyimide-polycaprolactone (PCL-PI-PCL) was first synthesized and used to disperse SWNTs in a low boiling point solvent (here we used tetrahydrofuran, THF) and fabricate the composite with epoxy resin. This triblock copolymer has good solubility and are highly effective in dispersing SWNTs in THF, as determined using UV-vis-NIR spectrophotometer, visual observation, and TEM, whereas the PI homopolymer was not so

effective in these aspects. For composite processing, new polymers are needed to disperse CNTs in common organic solvents. The synthesized PCL-PI-PCL triblock copolymer dispersed SWNTs (2 wt%) increased the tensile strength, modulus, and elongation at maximum stress by 74%, 35%, and 62%, respectively, as compared to the neat resin blend. As a control comparison, when only the dispersing agent is added to the epoxy resin, the overall tensile properties of the resin decreased.

To further improve the tensile properties of the SWNTs/epoxy nanocomposites, we fabricated another series of PI-derived block copolymers via ring-opening polymerization initiated from hydroxyl-terminated polyimide of lactide and allyl-bearing 2-methyl-2-(allyloxycarbonyl)propylene carbonate (MAC) to produce PLA-*b*-PI-*b*-PLA (TB1) and PMAC-*b*-PI-*b*-PMAC (TB2) which are polyester and poly(ester-carbonate)-derived, respectively. The allyl pendant group allows facile functionalization and we successfully made the third series of the epoxidized derivative of TB2, *i.e.* PMACEP-*b*-PI-*b*-PMACEP (TB3). We dispersed SWNTs in epoxy resin using these copolymer dispersants and evaluated the mechanical properties of the composite films. The optimal copolymer dispersant (TB3b), which has epoxy groups on the end blocks, can disperse 2% loading of SWNTs and the tensile strength, modulus, and elongation at maximum stress of the composite film increased by 40%, 34%, and 26%, respectively compared to neat epoxy resin. This new synthesis route of the triblock copolymer is applicable to diverse PI-based triblock copolymers with various desired functionalities. By introducing the allyl functional groups, the polymer can further react with other materials where the functional groups can then be easily changed to other functional groups.

The main achievement of this thesis is that we first apply chromium complexed SWNTs in polyimide composite films and get a reinforcement in the mechanical

properties, especially in modulus. Also, we design a series of triblock copolymers as polymer dispersants for carbon nanotube nanocomposites. The triblock copolymers have good solubility even in low boiling point solvent, and can achieved stable and homogenous CNT dispersion.

Chapter 1 Introduction

1.1 Background

Carbon nanotubes (CNTs) are high-performance materials that can be used as nanofillers material for polymer matrix composites reinforcement with good mechanical, electrical and optical properties. In particular, the mechanical properties of CNT composites can achieve a tensile strength over 100 GPa and a Young's modulus around 1000 GPa.¹ However, these properties depend critically on the fine dispersion of CNTs in the matrix to achieve good interfacial stress transfer. Strong van der Waals forces between carbon nanotubes make this task very challenging as carbon nanotubes can easily aggregate into bundles.² Use of both covalent and noncovalent functionalizations have been reported²⁻⁴ on assisting dispersion of carbon nanotubes. While covalent functionalizations can improve the dispersion and interfacial strength, the covalent bonds typically destroy the long-range π conjugation of CNTs which lower their conductivity and strength.⁵ Noncovalent CNT functionalizations are usually realized through physical absorption without disrupting the intrinsic structure of CNTs.^{6, 7} Recently, conjugated polymers and block copolymers attracted much attention.⁸ Conjugated oligomers and polymers can form π - π stack interactions with carbon nanotube walls, so that block copolymers having non-conjugated terminal blocks located at the outer surface of CNTs confer good solubility and stability in a wide range of organic solvents and host polymer matrices.⁹

1.2 Objectives of thesis

The field of organometallic polymer has emerged from a variety of disciplines such as organic chemistry, polymer chemistry, inorganic chemistry and material

engineering. The combination of metal (mostly transition metal) and organic units renders the polymers exhibit metal-like behavior, thus they may have special electrical, magnetic, mechanical or optical properties.^{10, 11} In covalent functionalization, the sp²-hybridized carbon atoms of CNT are converted to sp³ hybridization; breaking the p-conjugation length in this manner is a route for band-gap engineering of CNT.¹² In organometal complexation reactions, the vacant d-orbitals of a transition metal can overlap with and accept electron density from the occupied p-orbitals of CNT, resulting in the coordination of the metal atom to individual benzenoid aromatic rings of CNT and in bis-CNT metal sandwich complexes so that it is possible to electronically conjugate adjacent CNTs.¹³ The organo-metal is anticipated to provide a much milder modification of the electronic structure of CNT than covalent bond formation; as a result, the metal coordination site on the CNT surface is expected to be liable.¹⁴ We anticipate that such a complex will have a better load transfer compared to the conventional modified CNT. In this thesis, we introduce the organometallic approach to functionalize nanotubes and its application to composites.

In a previous study from Yuan Wei et al., polyimide (PI) has been reported to be a very good dispersant for carbon nanotubes because of the strong π - π interactions with CNTs side wall.^{15, 16} However, its poor solubility and incompatibility with other matrix limits its application. Polyimide or its precursor, poly (amic acid), can only be soluble in a few high boiling point solvents (like DMF, DMAc, NMP, etc.), which are hard to remove after casting the composite films. The residue solvent in the composites may introduce some voids and weaken the mechanical properties of the composites. Hence, we design a novel triblock copolymer using PI as center block and polycaprolactone (PCL) as side blocks. Such ABA block copolymer can be synthesized through attachment of active groups at the two ends of the center block macroinitiator, and then

initiating the polymerization of the side blocks.^{17, 18} The center block part is designed to disperse the carbon nanotubes and the two side blocks are chosen to provide good solubility in solvents. Polyester (such as polycaprolactone or polylactide) and poly(ester-carbonate) are compatible with a range of solvents and materials (such as epoxy and tetrahydrofuran solvent) and are often used as additive for resins to improve their processing characteristics and their end use properties.¹⁹ Through chemical functionalization of these polymers, more polymer matrices can also be applied.²⁰ A third triblock copolymer series was designed to disperse the CNTs in tetrahydrofuran (THF) with higher compatibility with epoxy resin, specifically poly(lactide)-*b*-polyimide-*b*-polylactide (PLA-PI-PLA), poly(2-methyl-2-(allyloxy-carbonyl)-propylene carbonate) (MAC)-*b*-polyimide-*b*-poly(MAC) (PMAC-PI-PMAC), and the epoxidized derivative of PMAC-PI-PMAC (labelled as PMACEP-PI-PMACEP).

1.3 Organization of thesis

This dissertation is divided into 6 Chapters. Chapter 1 is introduction to the thesis. Chapter 2 presents the literature review of polymer matrices, CNTs, and CNT/polymer composites, and introduces the organometallic polymers and block copolymers. Chapter 3 details the synthesis of SWNT-chromium-polymer complex and its application in composites. Chapter 4 describes the design and synthesis of polycaprolactone-polyimide-polycaprolactone (PCL-PI-PCL) triblock copolymer. The dispersion of SWNTs with the synthesized triblock copolymer and mechanical properties of SWNT/ PCL-PI-PCL/Epoxy composites were investigated. Chapter 5 further discusses the noncovalent functionalization of SWNTs via a series of other triblock copolymers (PLA-PI-PLA, PMAC-PI-MAC, and PMACEP-PI-PMACEP) and comparison of their mechanical reinforcement in epoxy composite films. Chapter 6 presents the conclusion of this dissertation and recommendations for future works.

Chapter 2 Literature Review

2.1 Polymer matrices

A composite is defined as a combination of two or more materials with a distinguishable interface. Polymer matrix composites (PMCs) typically comprise fillers bound by an organic polymer matrix. The matrix binds the fillers and transfers loads between them. The integration of two or more components is provided by a continuous polymer matrix, which usually fulfils the following criteria:

1. Provides shape and size stability of the material.
2. Fixes a given distribution of fibers relative to each other.
3. Gives the material deformation stability under thermal and mechanical loading up to the level given by the performance specifications.
4. Redistributes the external action on all fillers in a composite material, including broken and distorted ones.
5. Improve resistance and stability to the medium to sustain the environment it is intended. ²¹

The polymer matrix can be classified as either thermoset or thermoplastic based on their properties.

2.1.1 Thermosetting resins

Thermosetting resins include polyesters, vinylesters, epoxies, bismaleimides, and polyamides. Epoxy resins cover a broad class of chemicals with various physical and mechanical properties. Thermosetting resins are typically isotropic, and normally exist as brittle solids because of their three-dimensional crosslinked structure, which tends to have high dimensional stability, high-temperature resistance, and good resistance to

solvents. Recently, considerable progress has been made in improving the robustness and maximum operating temperatures of thermosets.

2.1.2 Thermoplastics

Thermoplastic resins, referred to as engineering plastics, include non-crosslinked linear polyesters, polyetherimide, polyamide/imide, polyphenylene sulfide, polyether-etherketone (PEEK), and liquid crystal polymers. Thermoplastics offer great promise for manufacturing applications, because they facilitate easier and faster heating and cooling of a material to tune its properties. Thus, thermoplastic matrices are attractive to high-volume industries such as the automotive industry. Thermoplastics are primarily used with discontinuous fiber reinforcements such as chopped glass or carbon/graphite and clay particulates.

Unlike thermosetting resins, thermoplastics are not cross-linked. They derive their strength and stiffness from the inherent properties of their linear polymer backbone and high molecular weight. The chain entanglements act as physical crosslinks to impart strength.²²

2.1.3 Polyimide (PI)

Polyimide has been widely applied in many fields. Its good properties such as heat resistance, chemical resistance and good mechanical properties have attracted much attention. During these years, many kinds of composites have been made using polyimide as matrix to improve the mechanical properties with different fillers such as carbon-nanotubes.^{15, 23}

2.1.4 Epoxy (EP)

A wide variety of composites can be made using epoxy as a matrix as shown in **Table 2.1.**²⁴

Table 2.1 Various types of epoxy composites and the manufacturing process²⁴

Composites	Reinforcement	Process
Fibre reinforced plastic composite	Glass fibre, carbon, Kevlar fire, basalt fibre	Wet lay-up and compression moulding, prepreg lay-up with vacuum bagging and autoclave curing, filament winding with oven curing, pultrusion, resin transfer moulding (RTM), liquid composite moulding, structural reaction engineering moulding
Particulate microcomposite	Silica, carbon black, calcium carbonate, glass beads, glass balloons, silicon carbide	Mechanical mixing and casting, compression moulding, matched-die moulding
Nanocomposite	Nano silica, nanocalcium carbonate, nanoclay, carbon nanofibers, carbon nanotubes	Mechanical mixing and sonication followed by casting or compression moulding

Cross-linked epoxies exhibit outstanding properties, and thus, serve as the standard option for diverse applications such as preparing adhesives, coatings, and composites of structural materials. The use of carbon nanotubes (CNTs) as fillers can impart outstanding mechanical, thermal and electric properties. Innovations in formulation and processing techniques have produced improved adhesives.²⁵

However, the epoxy composites are highly susceptible to internal damage under low-velocity impact due to the inherent brittleness of the cured resin, which may lead to severe problems. Thus, for high-performance applications, the improvement of damage tolerance of epoxy composites by enhancing their impact strength is essential and has been the subject of investigation in this field.²⁴

2.2 Carbon nanotubes (CNTs)

2.2.1 CNT structure

Carbon nanotubes (CNTs) are a relatively new class of one-dimensional (1-D) nanomaterials of the carbon material family. They can be viewed as single or nested concentric tubes formed by rolling two-dimensional (2-D) graphene sheets, with ends that may be capped by hemifullerenes. According to the number of graphene sheet layers, CNTs can be classified into single-walled nanotubes (SWNTs)²⁶ and multi-walled nanotubes (MWNTs).²⁷ SWNTs have diameters ranging from 0.4 to 3 nm²⁸ and the lengths in the order of micrometers.

The way how the graphene sheet is rolled into a nanotube determines nanotube chirality, which is defined by the chiral vector, $C_h = na_1 + ma_2$, where a_1 and a_2 are unit vectors and n and m are integers (**Figure 2.1 A**).²⁹ According to the nanotube chirality, SWNTs can be classified as follows: armchair ($n = m$), zigzag ($n = 0$ or $m = 0$) and chiral (all others) (**Figure 2.1 B**).³⁰ The chirality of SWNT determines their electrical properties (**Figure 2.1 C**).³⁰ All armchair nanotubes (n, n) have band gaps of 0 eV and thus show metallic properties. For other nanotubes with chiral indices (n, m), when $n-m=3p$ (where p is an integer and $\neq 0$), they are semimetallic with a band gap of a few meV, otherwise they are semiconductors with a band gap ranges from 0.5–1 eV.³¹ MWNTs comprise an array of concentric layers of individual carbon nanotubes²⁷ with an interlayer distance of approximately 0.34 nm³² (**Figure 2.1 D**). Their diameter depends on the total number of graphene sheets, ranging from 5 to 20 nm, while the length can be a few millimeters.

Figure 2.1 A) A schematic diagram showing formation of a SWNT by rolling-up graphene strips at various angles.²⁹ B) Schematic representation of (a) armchair, (b) zigzag and (c) chiral SWNTs.³⁰ C) Chiral vectors specified by the pairs of integers (n, m) for SWNTs. Small dots represent semiconducting tubes while encircled dots are for metallic tubes.³⁰ D) TEM images of MWNTs with different layers.²⁷

2.2.2 CNT synthesis

The following three techniques are commonly used to synthesize carbon nanotubes, i.e. arc discharge,²⁷ laser ablation³³ and chemical vapor decomposition (CVD).³⁴ The comparison of these techniques is listed in **Table 2.2**.³⁵ In the arc discharge and laser ablation techniques, solid carbon is first evaporated to form a hot gaseous carbon feedstock, which produces CNTs through condensation^{27, 33}. These two methods provide good control over the quality of the CNTs but are difficult to scale up. Most commercially available, high-quality CNTs are produced by arc discharge

technique because of its lower cost compared to the laser ablation process. The CVD method involves the decomposition of hydrocarbons over a transition metal catalyst (e.g. cobalt, nickel or iron) to form CNTs. CVD methods include fixed beds,³³ fluidized beds,³⁵ floating catalysts³⁶ and combination methods,^{37, 38} etc. The CVD technique is effective for a large scale preparation of SWNTs and MWNTs, and many companies have applied them to produce large quantities of CNTs.

All synthesis techniques yield mixtures of nanotubes with various diameters, lengths, chiralities, and defect densities as well as impurities. Thus, nanotube properties vary significantly depending on the synthesis protocol. The impurities found in synthetic CNTs are mainly amorphous carbon and metal catalysts. Purification of CNTs is typically performed in two steps, involving: thermal oxidation of amorphous carbon followed by acid treatment to remove catalyst particles.^{39, 40}

Table 2.1 Comparison of the techniques for nanotube synthesis³⁵.

Method	Arc discharge		Laser ablation		CVD
description	arc evaporation of graphite in the presence of inert gas; CNT formed on electrodes during quenching		vaporization of graphite target by laser; CNT formed on receiver during quenching		decomposition of hydrocarbons over transition metal catalyst to form CNT
operation temperature	> 3000°C		> 3000°C		< 1200°C
operating pressure	50–7600 Torr	generally under vacuum	200–750 Torr	generally under vacuum	760–7600 Torr
advantages	good quality CNTs		good quality CNTs; single conformation SWNT formed		easy scale up; synthesis on templates possible
disadvantages	difficult to scale up		difficult to scale up; expensive		quality of CNT not as good

2.2.3 CNT properties

The carbon-carbon bonds of CNTs are sp^2 bonds and they can provide excellent mechanical properties. Based on computer simulation result and experimental result, the Young's modulus can achieve 1.5 TPa⁴¹ and tensile strength 50-200 GPa⁴². Besides the excellent mechanical properties, other physical properties of carbon materials are listed in **Table 2.3**.⁴³ The superior properties of CNTs led to interesting applications in many areas.

Table 2.1 Physical properties of different carbon materials.⁴³.

Property	Graphite	Diamond	Fullerene	SWCNT	MWCNT
Specific gravity (g/cm ³)	1.9–2.3	3.5	1.7	0.8	1.8
Electrical conductivity (S/cm)	4000 ^p , 3.3 ^c	10^{-2} – 10^{-15}	10^{-5}	10^2 – 10^6	10^3 – 10^5
Electron mobility (cm ² /V s))	2.0×10^4	1800	0.5–6	$\sim 10^5$	10^4 – 10^5
Thermal conductivity (W/(m K))	298 ^p , 2.2 ^c	900–2320	0.4	6000	2000
Coefficient of thermal expansion (K ⁻¹)	-1×10^{-6p} 2.9×10^{-5c}	$(1 \sim 3) \times 10^{-6}$	6.2×10^{-5}	Negligible	Negligible
Thermal stability in air (°C)	450–650	<600	~ 600	>600	>600

p: in-plane; c: c-axis.

2.3 Organometallic polymer

The Organometallic polymers, also known as metallopolymers, maybe classified according to their structure and composition. One way of classifying such polymers involves grouping them into metal incorporated on the side-chain and main-chain polymers. Usually, the main-chain metal-containing polymers are preferable because

the influence of metal is more significant on the backbone, including their thermophysical properties and the conjugation pathway. Here we give some common examples of different kinds of metallopolymers.¹¹

2.3.1 Polygermanes and polystannanes

Polystannanes and polygermanes are heavier Group 14 congeners of polysilanes (**Figure 2.2**),⁴⁴ but their HOMO-LUMO gaps are lower than polysilanes. The polygermanes contain germanium and the polystannanes contain tin atoms on the main chain. Such polymers can dissolve in many organic solvents, and are very sensitive to light, especially, in solution and in the presence of oxygen.⁴⁴

Figure 2.2 Polysilanes, polygermanes and polystannanes.⁴⁴

2.3.2 Metallocene polymers

Ferrocene-containing polymers have provided access to a class of organometallic compounds commonly known as the metallocenes. Transition metal with π -bonded aromatic ring system is both thermally and electrochemically strong. Such segment can be seen in many kinds of polymers. They also have higher molecular weight. Their refraction indices can also be varied by changing the main-group element so that they can be used in photonic devices.

Ferrocene has 18 valence electrons. To prepare ferrocene-containing polymers, cyclopentadienyl group must be linked to the polymer. The ferrocene units can be pendants or side chains of the polymer (**Figure. 2.3**).

Figure 2.3 Ferrocene and ways of incorporating it in a polymer.

2.3.3 Polyyne rigid-rod organometallic polymers

Such polymers have late second- and third-row transition metal ions (mainly Pt(II) and Pd(II)) as part of a polymeric linear chain.⁴⁴ These ion prefer square planar geometric structures. Thus, the metal centers covalently bonded to a highly ethylated main chain, like rigid rod. The “condensation reaction between the metal salt and the diyne is catalyzed by Cu (I) salts and is usually carried out using amines such as diethylamine as solvents under reflux conditions”.⁴⁴ These polymers have some good properties such as air-stable, high molecular weight, good solubility and nonlinear optical properties, which make it possible for nanodevice applications.

2.3.4 Coordination polymers

They are coordination compounds with metal cation centers linked by organic ligands. It can be one-dimension, and can also crosslinked to two or three dimensions. The dimensionality usually depends on the coordination number of the metal center. In order to add metal to the polymer chain, three main methods are utilized: addition, condensation and coordination.

Addition polymerization of unsaturated organic molecules is an important process for many organo-metallic polymers. Such route has thermodynamic driving force to convert π -bonds to more stable σ -bonds and chained with active units as intermediates.

Condensation method to synthesize the polymer is through condensation reaction. The metal is pre-connected with one or more organic groups, with reaction sites around the metal.

Coordination method is applied to add metals to an already formed polymer, by coordination bonds between the metal and the organic ligands. There are three common routes as reported: 1) condensation or addition of the metal complex; 2) chelate groups coordination with a metal ion; 3) metal donor atom reaction to form polymer.

Generally, organo-metallic polymers are soluble in fewer solvents than classical organic polymers. The metallic dopants usually lead to low solubility of the organometallic polymers, which is due to the organometallic bonds. As these polymers have both polar and non-polar parts, it could be hard to find a good solvent. The polymers are also highly cohesive with some of them having crystalline microstructure.¹⁰

The addition of metals may enhance the conductivity of polymers as the strong $d\pi$ - π interactions conjugate throughout the material and form metallic-like or semi-conductive band structures. The transition metals can also change the oxidation state or coordination number and thus change the conductivity of the polymer. Such property can be used to make switchers or sensors.

Due to their special properties, metallopolymers have a variety of applications such as solar cells, sensors, nanoscience, and catalysis. Metal catalysis supported on the polymers may have advantages of great efficiency, selectivity and separation. The reactions include hydrocarboxylation, hydroformylation, linear oligomerization, cyclooligomerization, and decarboxylation.⁴⁵

2.4 Block copolymers

Block copolymers are a fascinating class of materials that comprise at least two thermodynamically incompatible polymer chains, thus generating a rich variety of microstructures in bulk and in solution.⁴⁶ The variety of microstructures gives rise to materials with “applications ranging from thermoplastic elastomers and high-impact plastics to pressure-sensitive adhesives, additives, and foams. In addition, block copolymers are strong candidates for potential applications in advanced technologies such as data storage, drug delivery, and photonic crystals.”⁴⁶ Owing to the interesting properties of block copolymers, there have been many interesting developments in their synthesis, properties, and applications.⁴⁷

2.4.1 Block copolymer synthesis

Advances in the synthesis of linear (e.g., AB diblocks, ABA and ABC triblocks, ABCD tetrablocks, (AB)_n multiblocks etc.) and nonlinear (star-block, graft, miktoarm star, H-shaped, dendrimer-like, and cyclic copolymers) block copolymers have been recently achieved.⁴⁸

There are typically two methods for synthesizing of AB diblock copolymers: (a) sequential addition of monomers; and (b) coupling of two appropriately end-functionalized chains. An essential consideration for the first method is the order of monomer addition. The active chain of the first monomer must efficiently initiate the polymerization of the second monomer. Another requisite is that the conversion of the first monomer must be quantitative to control the molecular weight.

The synthesis of ABA triblock copolymers can be achieved using one of the following methods: (a) three-step sequential addition of monomers; (b) two-step sequential addition of monomers followed by a coupling reaction with a suitable

difunctional linking agent; and (c) use of a difunctional initiator and a two-step sequential addition of monomers. The third method is versatile for the synthesis of triblock copolymers, because it requires a two-step reaction without fractionation or other purification steps. However, the main limitation of this method is the choice of the difunctional initiator, which must initiate the bidirectional polymerization of the desired monomer at the same rate.⁴⁸

2.4.2 Phase behavior and morphologies of block copolymers

Block copolymers comprise different polymer chains. They can form different structures depending on their number of blocks, the composition, and the way linked together (linear, branched, star-like or cyclic) with characteristic lengths. This self-organization into ordered structures is called morphologies and it has attracted considerable studies during these years.^{49, 50} Besides the pure block copolymers, their blends with other fillers have also attracted much interests. By changing the temperature to control the thermodynamics or by adding low boiling points solvents to block copolymers, homopolymers or other block copolymers, the block copolymer morphologies can be manipulated.⁵¹

The simplest block copolymers are linear diblock copolymers (AB), show cubic packed spheres, hexagonal packed cylinders, double gyroid and lamellae, or their inverse phases (**Figure 2.4**).

Figure 2.4 Morphologies of linear diblock copolymers (AB)

“The choice of the appropriate chemistry, composition and architecture of the immiscible blocks can lead to morphology control on the nanoscale. The generated structures can be further altered by selective treatment of one phase or by the use of physical forces, e.g. shear deformation or electrical fields. Compared to linear AB diblock copolymers, the number of morphologies for linear ABC triblock terpolymers is more than doubled leading to the formation of nanostructures as complex as rings or even helices. More structural variations are accessible when the block polymers are blended or their architecture is changed from linear to more complex array.”⁵²

2.4.3 Block copolymer applications

The most common block copolymers, thermoplastic elastomers (TPEs), have both thermoplastic and elastomeric properties so that they can be used for wine bottle stoppers, jelly candles, outer coverings for optical fiber cables, adhesives, bitumen modifiers, or in biomedical technology.⁵³ Polyurethanes are first commercially available TPEs. Their extensive structure/property diversity and bio-compatible properties bring interesting biomedical applications.⁵⁴ Recently a tetrafunctional multigraft copolymer comprises of polyisoprene backbone (providing elasticity) and two polystyrene branches (22% PS content) have been reported, showing enhancement in both strength and strain at break.⁵⁵ Such examples inspire us to develop novel functional materials by applying block copolymers in the composites.

2.5 CNT/polymer nanocomposites

2.5.1 Dispersion and functionalization of CNTs

The properties of polymer composites strongly depend on filler dispersion and filler/matrix interfacial interaction. However, CNTs typically form agglomerates

because of van der Waals forces.⁵⁶ The nanotube agglomerates reduce the contact of the nanotube surface with the polymer matrix, and consequently, decrease stress transfer. Thus, good dispersion of carbon nanotubes is essential to make high performance composites. To improve nanotube dispersion and avoid the CNT agglomeration, it is necessary to functionalize CNTs. Several strategies have been reported including defect functionalization, covalent and noncovalent approaches (Figure 2.5).⁵⁷

Figure 2.5 Functionalization possibilities for SWNTs: A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent exohedral functionalization with surfactants, D) noncovalent exohedral functionalization with polymers, and E) endohedral functionalization with, for example, C₆₀. For methods B–E, the tubes are drawn in idealized fashion, but defects are found in real situations.⁵⁷

2.5.1.1 Covalent functionalization

As carbon nanotubes are constructed with sp^2 -hybridized carbon atoms, the side walls of the carbon nanotubes are reactive to some chemicals. The traditional ways of

covalent functionalization are 1) acid oxidation and subsequent derivatization of defect sites and end-caps;⁵⁸⁻⁶¹ 2) direct sidewall functionalization using reactive species.⁶²⁻⁶⁶ to convert the sp^2 carbon atoms to sp^3 carbon atoms. Some reactions are summarized in **Figure 2.6**. The attached functional groups, such as $-OH$, $-COOH$, or $-Cl$, can be further reactive to specific materials, or can improve the stability in specific solvents. However, the origin side-wall structure is disrupted, so the electrical properties are influenced.⁶⁷

Figure 2.6 Overview of possible addition reactions for the functionalization of the nanotube sidewall.⁶⁸

2.5.1.2 Non-covalent functionalization

Noncovalent functionalization involves physical adsorption/wrapping of surfactants or polymers on nanotube surface. This method is interesting because it can effectively disperse CNTs without disturbing the nanotube π system and compromise

the physical properties of CNTs. Numerous studies have found that some molecules, including surfactants,^{69, 70} aromatic compounds^{71, 72} and polymers⁷³⁻⁷⁵ can adsorb onto CNTs surface via noncovalent interaction (hydrophobic interaction, π - π interaction, and van der Waals interaction) both in aqueous and nonaqueous solvents.

Surfactants are proved to be useful CNT dispersants in water. The surfactants can be anionic, cationic, and non-ionic.⁷⁶ Anionic surfactants such as sodium dodecylsulfate (SDS)⁷⁷ and sodium dodecylbenzene sulfonate (NaDDBS)⁷⁸ are commonly used. The CNTs are surrounded by hydrophobic components of the corresponding micelles. Surfactants with aromatic groups in the hydrophobic parts can get better dispersion due to the stronger interaction (like NaDDBS and Triton X100) (**Figure 2.7**).

Figure 2.7 Schematic representation of how surfactants may adsorb onto the nanotube surface.⁷⁹

Other non-covalent CNT dispersants, for example, conjugated polymers, can be applied in organic solvents and form supramolecular complexes with CNTs. A variety of conjugated polymers have been reported to have π - π interaction with carbon nanotube side wall, such as polybenzimidazole (PBI), poly(aryleneethynylene)s (PPE), p-phenylenevinylene (PmPV) and some polyimides (**Figure 2.8**).

Figure 2.8 (a) Polybenzimidazole (PBI) is shown to individually dissolve/disperse single-walled carbon nanotubes (SWNTs) in N,N-dimethyl-acetamide (DMAc).⁸⁰ (b) A non-wrapping approach to noncovalent engineering of carbon nanotube surfaces by introducing alkyl side chain on poly(aryleneethynylene)s (PPE) rigid polymer.⁸¹ (c) poly (p-phenylenevinylene-co-2,5-dioctyloxy-mphenylenevinylene) (PmPV-co-DOctOPV).⁸² (d) Aromatic/aliphatic polyimides prepared from 2,7-diamino-9,9'-dioctylfluorene (AFDA) and aromatic dianhydrides.⁷³

In previous research of our group, Yuan Wei has synthesized a series of polyimides with different side chains^{4, 16} or poly (amic acid)¹⁵ for dispersing carbon nanotubes via non-covalent functionalization. For reinforcement of cyanate ester/epoxy composite, polyimide-graft-bisphenol A diglyceryl acrylate (PI-BDA) is highly effective in dispersing SWNTs into individual nanotubes or small bundles. The designed comb-like polymer dispersant interacts noncovalently with nanotubes on the main chain but reacts with the thermo-setting matrix because of the reactive epoxy groups on the side chains.

2.5.2 Charge transfer

Three types of nanocarbons have emerged in past years, fullerenes, carbon nanotubes and graphene. They are different dimensions network of carbon atoms with fascinating properties. One of the characteristics is molecular charge-transfer involving these nanocarbons. “Both graphene and single-walled carbon nanotubes (SWNTs) interact with electron donor and acceptor molecules giving rise to significant changes in the electronic structure”.⁸³

The doping strategy contains electrochemical and chemical doping. The electronic structure and phonon frequencies of SWNTs are affected on doping with electrons or holes.⁸³ The chemical doping involves covalent or non-covalent functionalization.

Raman spectroscopy is a powerful tool to study charge transfer in SWNTs. Adsorption of electron donating and accepting molecules cause shifts in the Raman peak frequencies, which are proportional to the amount of carriers injected.⁸⁴ The Raman band of SWNTs centered around 1580 cm^{-1} (G-band) exhibits a feature around $\sim 1540\text{ cm}^{-1}$ which is characteristic of metallic SWNTs.⁸⁵ In addition to these two bands, a third peak called D band typically appears at 1330 cm^{-1} in both the SWNT and graphene Raman spectrum due to disorder.

2.5.3 Fabrication of CNT/polymer composites

As we mentioned above, the dispersion of carbon nanotubes is of great importance during the fabrication process. Currently there are several methods to maintain the dispersion when mixing the CNTs and polymer matrix, such as solution mixing, melt mixing and in-situ polymerization.⁷⁹

2.5.3.1 Solution mixing

In this method, CNTs are dispersed in suitable solvents, while CNT dispersion and soluble polymer matrix are mixing thoroughly, the solvent is removed to form a CNT/polymer composite either by evaporation or precipitation. CNTs are usually functionalized by either covalent or noncovalent approaches; and high power ultra sonication is widely used to debundle the CNTs and get a homogeneous dispersion. This method is the most common method because agitation of CNTs in a solvent facilitates CNT dispersion and prevents CNT re-aggregation.⁸⁶⁻⁹⁰

2.5.3.2 Melt mixing

In solution blending method, the polymer must be soluble in at least one solvent. In contrast, melt/mixing do not need any solvent. It can be used for insoluble polymers, and can save large amount of solvents during processing. This method is practically useful for some high molecular weight thermoplastic polymers. During this process, CNTs are mechanically dispersed into a polymer matrix using a high temperature and high shear force mixer or compounder.⁹¹

2.5.3.3 In-situ polymerization

In this polymerization approach, CNTs are dispersed in monomers followed by polymerization. Covalently functionalized nanotubes are usually used, which lead to strong interaction with the polymer matrix, to provide high mechanical reinforcement through effective load transfer. Hu et al. synthesized MWNT-reinforced polyimide nanocomposites by in-situ polymerization of monomers in the presence of acylated MWNTs, as shown in Scheme 2.1.⁹²

Scheme 2.1 Outline of the preparation of MWNT-polyimide nanocomposite films.⁹²

2.5.4 Applications of CNT/polymer composites

The outstanding properties of carbon nanotubes enable the potential usage in controlling other nanoscale structures, an interesting property that could have an important role in nanotechnology engineering.

2.5.4.1 Nanotube networks cut polymer flammability

Researchers have found that if carbon nanotubes in a polymer matrix form a “jammed network” structure they can act as more effective flame-retardant additives than nanoclay particles, such that the material as a whole behaves rheologically like a gel. The addition of nanotubes also improves the mechanical properties and electrical conductivity of the polymers.⁹³

Nanoclays and nanotubes could replace halogenated flame-retardant additives, a number of which are banned because of the damage they cause to the environment. The resulting nanocomposites could have applications in packaging, electronics, construction and the aerospace industry.

2.5.4.2 Transparent conductive films containing CNTs

CNT-based transparent conductive films may be used as a replacement for the brittle and expensive indium tin oxide (ITO) coated films currently used in such products as touch screens, LCD displays, solar cells, and solid state (OLED) lighting.⁹⁴

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Our interest here is to investigate the mechanical properties enhancement after dispersion of SWNTs in polymer matrix. The objectives is to design a novel polymer dispersant which do not break the interior structure of SWNTs and have good solubility in low-boiling-point solvent and compatibility with polymer matrices. These features should improve the mechanical properties of the fabricated composites.

Chapter 3 Chromium Polymer

Functionalized Single-Walled Carbon

Nanotubes for Polyimide Composites

3.1 Introduction

Carbon nanotubes (CNTs) are high-performance materials used in polymer matrix composites as they show good mechanical properties. For example, CNTs show high tensile strength (over 100 GPa) and Young's modulus (around 1000 GPa).¹ However, the exploitation of properties depends on the uniform dispersion of CNTs in the matrix and good interfacial stress transfer. Strong van der Waals forces between the high surface area carbon nanotubes make this task challenging.² To achieve this goal, both covalent and noncovalent functionalizations have been reported.²⁻⁴ Covalent functionalizations can improve the dispersion and interfacial strength but may lower their conductivity as the covalent bonds destroy the long-range π conjugation of CNTs.⁵ Noncovalent functionalizations are usually realized through physical absorption without disrupting the intrinsic structure of CNTs.^{6, 7}

We attempt to use the organometallic approach to functionalize nanotubes. The combination of metal (mostly transition metal) and organic unit makes the resulting organometallic polymers possess metal-like behavior, thus they may have special electrical, magnetic, mechanical or optical properties.^{10, 11}

In a typical covalent functionalization of nanotubes, the sp^2 hybridized carbon atoms of CNT are converted to sp^3 hybridization; breaking the p -conjugation which is commonly employed for the band-gap engineering of CNT.¹² In organometal

complexation reactions, the vacant d-orbitals of a transition metal can overlap with and accept electron density from the occupied p-orbitals of CNT. This results in the coordination of the metal atom to the π -conjugated aromatic rings of CNT and also form bis-CNT metal sandwich complexes (one metal complex with two side-wall of CNTs on the two ends) so that it is possible to electronically conjugate with adjacent CNTs.¹³ The metal ions are anticipated to provide a milder modification without destroying the electronic structure of CNT like the covalent s-bond functionalization¹⁴ We anticipate that such a complex will have a better load transfer compared to the conventional modification of CNT because carbon-metal complex bond has stronger force compared with normal π - π van der Waals force which occurs in non-covalent functionalized materials.

Here we use chromium to complex with bipyridine-containing polymer and single walled carbon nanotubes. The chromium carbide is reported to react with carbon nanotubes.¹⁴ Three CO ligands can be replaced by side-wall of CNT, and the other three CO ligands can be replaced by the bipyridine structure. We expect that using this organometallic complex bonding can enhance the interaction between the carbon nanotubes and the attached polymer. In this way, the mechanical properties of the composites will be improved.

3.2 Experimental section

3.2.1 Materials

3,3'-Dihydroxy-4, 4'-diaminobiphenyl (HAB, 97%), 4,4'-Diamino-2,2'-bipyridyl (BDA) were obtained from Tee-Hai. Pyromellitic dianhydride (PMDA, 97%), 4,4'-Oxydiphthalic anhydride (ODPA, 97%), 4,4'-diaminodiphenyl sulfone (ASO),

Glycidyl 4-nonylphenyl ether (GNE, technical grade, scheme 2), 4-dimethylaminopyridine (DMAP, 99%), N,N'-dimethylacetamide (DMAc), xylene, dimethyl sulfoxide (DMSO), N,N'-dimethylformamide (DMF), and methanol were obtained from Sigma-Aldrich. DMAc were distilled over calcium hydride before use. All other chemicals were used as received. SWCNTs (ASP-100F) were purchased from Hanwha Nanotech Corporation and were purified with thermal oxidation at 300°C for 2 h before use.

3.2.2 Synthesis of poly (amic acid) as the matrix

The synthesis of poly (amic acid) was achieved using a method reported earlier.⁴ Typically, the monomer HAB (2.16 g, 10 mmol) was dissolved in 50 mL freshly distilled DMAc, after which ODPA (2.94 g, 10 mmol) was added at 0°C and the mixture was stirred at room temperature for 24 h (Scheme 3.1).⁴ A viscous poly (amic acid) (PAA) solution was formed and then kept in a fridge until use. For further characterization, some polymer was dried using a rotoevaporator. The molecular weight of PAA was 4.56×10^5 g/mol (Mw) and the polydispersity index is 1.33 determined by GPC.

Scheme 3.1 Synthesis of PAA and thermal imidization for polyimide films.

3.2.3 Synthesis of poly (amic acid)-chromium-CNT complex

2 mmol 4,4'-diaminodiphenyl sulfone (ASO) and 0.5 mmol BDA were added into 10 mL THF, after degassing with argon for some time, 2.5 mmol dianhydride was added. The mixture was stirred at room temperature for 24 h under argon.

The resulting poly (amic acid) with sulfone groups (here we marked as PAAS) solution in THF (2 mL) and SWNTs (20 mg) were mixed in THF (10 mL) and then degassed with argon for 15 min. Then $\text{Cr}(\text{CO})_6$ (22mg) was added and the reaction

mixture was heated at 72°C for 72 h in the dark under a positive pressure of argon, after which it was cooled to room temperature. The suspension was filtered through a PTFE membrane and the solid was rinsed with anhydrous ether. The resulting grey-color complex was left to dry overnight under vacuum in the dark (Scheme 3.2).

Scheme 3.2 Synthesis of PAAS-Cr-CNT complex.

3.2.4 Fabrication of composite film

The composite films were fabricated by solution casting method, using synthesized PAA as a matrix. A measured quantity of PAAS-Cr-CNT were dissolved in 1 mL DMAc. Then, 100 mg PAA was added in the CNT solution and subsequently sonicated with tip sonicator (100 W, 65%, Vibra-Cell, Sonics) at 0°C for 30 min.

The solutions were then drop-casted onto a glass plate and casted using a doctor blade followed by solvent removal by heating at 50°C followed by further drying in vacuum oven overnight. Lastly, the drying process is finished with a consecutive sequence of heating at 100°C for 2 h, 150°C for 1 h, and 200°C for 30 min respectively. After cool down to room temperature, the films were carefully peeled off from the glass substrates. The resulting poly (amic acid) films are thermal imidized to polyimide (PI) films. Tensile properties of neat PI (ODPA-HAB) film and the composite films with various SWNT loadings were tested and the comparison data are summarized in **Table 3.1**. We further tested the two films after annealing by heating slowly to 250°C in argon. The mechanical properties of annealed films are given in **Table 3.2**.

Table 3.1 Mechanical Properties of Neat PI and PAAS-Cr-CNT/PI Composite Films

Films	Strenth [Mpa]	Modulus [MPa]	elongation[%]
Neat PI(ODPA-HAB)	113.79±15.97	3197.17±713.48	19.27±17.39
2.8% PAAS-Cr-CNT (0.34% CNT)/PI	112.17±6.89	3676.34±514.99	7.702±2.307
5.6% PAAS-Cr-CNT (0.68% CNT)/PI	111.08±14.74	4605.98±533.39	4.97±1.86
8.2% PAAS-Cr-CNT (1% CNT)/PI	115.62±9.47	4681.25±441.74	6.73±2.21

16.4% PAAS-Cr-CNT (2% CNT)/PI	109.55±8.34	4773.02±576.37	4.74±0.94
24.6% PAAS-Cr-CNT (3% CNT)/PI	93.96±7.22	5479.87±867.33	2.54±0.87

Table 3.2 Mechanical Properties of Neat PI and PAAS-Cr-CNT/PI Composite Films after annealing to 250 °C.

Films	Strengthen [Mpa]	Modulus [MPa]	elongation[%]
Neat PI(ODPA-HAB)	122.92±9.15	3890.65±442.00	8.84±1.19
2.8% PAAS-Cr-CNT (0.34% CNT)/PI	118.89±7.45	4180.48±388.67	6.65±1.75
5.6% PAAS-Cr-CNT (0.68% CNT)/PI	122.30±17.13	4279.75±354.81	6.03±2.22
8.2% PAAS-Cr-CNT (1% CNT)/PI	108.24±14.47	4103.69±281.29	6.01±3.35
16.4% PAAS-Cr-CNT (2% CNT)/PI	124.84±9.02	5259.55±302.14	4.39±1.14
24.6% PAAS-Cr-CNT (3% CNT)/PI	99.69±8.09	4710.84±475.14	3.47±0.75

3.2.5 Characterization

¹H NMR spectra of PAA were measured with Bruker Avance 300 NMR spectrometer using deuterated dimethylsulfoxide (DMSO-d₆) as solvent. The molecular weight (M_w) and polydispersity (PDI) of PAA were obtained via gel permeation chromatography (GPC), using DMF with 0.03 M LiBr as eluent and polystyrene

standards as a reference. Raman spectra were performed on a Renishaw Ramanscope with HeNe laser at an excitation wavelength of 633 nm. FT-IR spectra were obtained on a Nicolet 5700 FT-IR instrument. UV-vis-NIR absorption spectra of the nanotube solutions were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer. Optical microscopy characterization of Cr-SWNT/PI composites was carried out on an Olympus SZX12 microscope. The dispersion of SWNTs in composite was examined with a JEOL JSM-6700F field-emission scanning electron microscope (FE-SEM).

Tensile properties of composite film were determined by an Instron model 5543 mechanical tester at room temperature with a 100 N load cell and a cross head speed of 2.5 mm/min. At least 10 samples were tested and the results were averaged.

3.3 Results and discussion

3.3.1 Synthesis of PAA matrix

The PAA (Scheme 3.1) was synthesized from ODP and HAB, using stoichiometric amounts to get high molecular weight. The GPC of PAA is shown in **Figure 3.1**. High molecular weight polymer contributes to good mechanical properties of the films casted.⁹⁶ The choice of monomers of the starting material for polyimide films has tremendous affect to its resultant properties.⁹⁷ Further choice of aromatic structures the ether linkage make the polymer matrix allow us to tune the resultant molecule to have the desire properties of both strong and flexible.^{98, 99} The molecular structure of the polymer was confirmed in NMR spectrum (**Figure 3.2**).

Figure 3.1 GPC curve of PAA.

Figure 3.2 ¹H NMR spectrum of PAA (*d*₆-DSMO, 25°C).

3.3.2 Design and synthesis of PAAS-Cr-CNT complex

The approach for synthesis of the organometallic dispersant and CNT complex is schematically depicted in Scheme 3.2. We choose chromium because its reaction with CNT in THF has been well known¹⁴ and the reaction between chromium and bipyridine ligand was also well studied.¹⁰⁰ The structures of the synthesized PAAS and chromium complex were confirmed by FTIR spectra (**Figure 3.3**). The spectra of PAA and PAAS-Cr-CNT showed the amic acid peaks at $3200\text{--}3500\text{cm}^{-1}$ ν COOH and NH, 1710 cm^{-1} ν C=O (COOH) and 1660 cm^{-1} ν C=O (CONH)⁹⁷, which confirms the grafting of PAAS on CNTs. In order to know the percentage of the chromium in PAAS-Cr-CNT complex, TGA of the complex is run in air from 50°C to 750°C (**Figure 3.4**). When the temperature increased to 750°C , the organic polymer and SWNTs are burned away resulting in weight loss is 64%. The remaining content is chromium oxide and the weight percentage is 36%. Thus, we can calculate that the chromium is 12 wt% in the complex PAA-Cr-CNT.

Figure 3.3 FT-IR spectra of PAAS-Cr-CNT complex, PAAS and CNTs.

Figure 3.4 TGA curve of PAAS-Cr-CNT complex in air.

To confirm the strong interaction between chromium and carbon nanotube, Raman spectra of CNTs and PAAS-Cr-CNT were compared in **Figure 3.5**. It is known that because of charge transfer, the Raman peaks of undoped carbon nanotube will be shifted after doping.¹⁰¹ Indeed, in the case of PAAS-Cr-CNT, the G band has shifted from 1592.79 (for SWNTs only) to 1593.78 cm^{-1} , and the 2D band has shifted from 2583.28 (for pure SWNTs) to 2592.95 cm^{-1} . The intensity of PAAS-Cr-CNT also enhanced by 300% in comparison with undoped carbon nanotube. This enhancement can also indicate the interaction between CNT and chromium.¹⁰²

Figure 3.5 Raman spectra of SWNTs and PAAS-Cr-CNT complex.

3.3.3 Dispersion of PAA-Cr-CNT complex in DMF

The dispersion of the PAAS-Cr-SWNTs complex was quantitatively evaluated through the absorption spectra measurement and Beer-Lambert law ($A = \epsilon lc$), where A is the absorbance at a particular wavelength (here we chose 500 nm), ϵ is the extinction coefficient, l is the path length (1 cm for our cell), and c is the concentration, respectively. To determine the extinction coefficient (ϵ), the absorbance of PAAS-Cr-CNT complex solution at different concentrations (0.0125, 0.025 and 0.05 mg/mL) were prepared by bath sonication for 30minute (1 and 1 second on/off) and their corresponding absorbance at 500 nm were plotted against chromium SWNT concentrations (**Figure 3.6**). The linear-least-squares fit to the data gave a slope of 24.78, which was used to calculate the extinction coefficient (i.e., $\epsilon = 24.78 \text{ mL mg}^{-1} \text{ cm}^{-1}$) for determination of chromium SWNT complex concentration (**Figure 3.6**).

Figure 3.6 (a) Absorption spectra of SWNT/chromium complex (mass ratio = 1:2) in DMF at different nanotube concentrations. (b) Absorbance of these dispersions at 500 nm. The straight line is a linear-least-squares fit to the data.

The 1 mg/mL solution of PAAS-Cr-CNT in DMF was prepared by tip sonication for 30 minute (1 and 1 second on/off) and the absorption at 500 nm was measured after centrifugation at 3000 rpm for 5 min and 6000 rpm for 5 min. The spectra of the starting materials were also recorded for comparison. For comparison, the same concentration of CNTs and PAAS in DMF were also sonicated and centrifuged under identical conditions.

The nanotube concentrations of PAAS-Cr-CNT and PAAS/CNT under different conditions, determined by measuring absorbance at 500 nm and calculated according to the Beer-Lambert law are shown in **Figure 3.7**. Immediately after sonication, both PAAS-Cr-CNT and PAAS/CNT have nanotube concentrations of 67~68 mg/L. After centrifugation at 3000 rpm and centrifugation at 6000 rpm, the nanotube concentration of PAAS-Cr-CNT decreases to 63 and 61 mg/L, respectively, which is much higher

than that of PAAS/CNT (13 and 7 mg/L, respectively), suggesting that the dissolution or dispersion of the CNT and polymer has improved after complexation reaction.

Figure 3.7 CNT concentrations of PAAS/CNT and PAAS-Cr-CNT under different conditions: immediately after sonication, and after centrifugation at 3000 rpm, 6000 rpm for 5min.

3.3.4 SWNT dispersion and interfacial bonding in composites

Representative photographs and optical microscope images of composite films containing different percentages of CNTs were taken and shown in Figure 3.8 and 3.9 respectively. The composite films with less than 2 wt% CNT exhibit good transparency and uniformity, while the composite with 3 wt% MWNTs is black and opaque. The optical microscope images were taken under 20 magnification, indicating homogeneous PAAS-Cr-CNT dispersion in PI matrix.

Figure 3.8 Photographs of composites films (a) pure PI film (b) composite film with 0.34 wt % CNTs (c) composite film with 0.68 wt % CNTs (d) composite film with 1 wt % CNTs (e) composite film with 2 wt % CNTs and (f) composite film with 3 wt % CNTs.

Figure 3.9 Optical micrographs of composite films: (a) pure PI film (b) composite film with 0.34 wt % CNTs (c) composite film with 0.68 wt % CNTs (d) composite film with 1 wt % CNTs (e) composite film with 2 wt % CNTs.

To further examine the nanotube dispersion and morphology in the films, the fracture surface of the composite films after mechanical testing were observed in FE-SEM. FE-SEM images of the fractured surfaces of composites with nanotube contents of 1-2 wt% are shown in **Figure 3.10**. The resultant SEM image showed that most of

CNTs were broken on the surface without any standing nanotubes indicating strong polymer-nanotube interfacial adhesion. However, the SWNTs are not dispersed individually because the complexation reaction connected both carbon nanotubes and polymer. The multiple reaction sites entangled the CNTs with polymer and no longer individually dispersed.

Figure 3.10 FE-SEM images of fracture surface of PI composite film with PAAS-Cr-CNT with different magnifications.

3.3.5 Mechanical properties of composite films

The tensile properties of neat PI and composite films with different SWNT loadings are listed in **Table 3.1**. As the weight percentage of SWNT is 12% in PAAS-Cr-CNT complex, which can be calculated from TGA curves, the measured weight percentage of PAAS-Cr-CNT 2.8%, 5.6%, 8.2%, 16.4% and 24.6%, indicated that CNT content should be 0.34%, 0.68%, 1%, 2% and 3% correspondingly. For the neat PI film, the tensile modulus is 3197 MPa and the strength is 113 MPa. In comparison to literature reported tensile values of polyimide, these modulus and strength are in the middle to high range of the published range, a result of the chosen diamine and dianhydride which gave the polyimide rigid structure.¹⁰³ As is shown in the table, when SWNTs are added, the elongation decreases compared to the neat PI resin without

SWNTs. Adding the SWNTs do not improve the tensile strength. However, we observed an increase of the tensile modulus when the SWNT loading increased from 0% to 2 wt%. On the other hand, when the SWNTs further increases to 3 wt%, the tensile property drops to 93.96 MPa, the elongation drops greatly and modulus increases 71.4% as the resultant resin becomes brittle and no longer flexible. We also observed that the chromium content also increased with increasing CNT loadings.

In order to further improve the mechanical properties of the resultant films, the films are annealed to 250°C to complete the imidization process and at the same time release the intrinsic stress. The mechanical properties of the films are tested and listed in **Table 3.2**. After annealing, both of the tensile strength and modulus properties increase for all the films, and the errors of elongation also decrease. However, the tensile strengths of the SWNTs-reinforced films did not increase compared to the neat polymer.

3.4 Conclusion

We have designed and successfully synthesized polymer-chromium-CNT complex, and have shown it to be effective in dispersing SWNTs and improving the mechanical properties, especially Yong's modulus, of the SWNT-reinforced polyimide composite films. The revealed polyimide composite films were prepared by solution casting and thermo-treatment. After annealing of the composite films, the mechanical properties increased. The films with 2 wt% functionalized SWNTs increased the tensile modulus composite by 35% (to 5.26 ± 0.31 GPa) over that of neat resin blend (with modulus 3.89 ± 0.45 GPa). The improvement of the mechanical property is attributed to the strong interaction between chromium functionalized SWNTs and the polymers. The FE-SEM of the fracture surfaces of the films and the Raman spectra can also show the

interaction and adhesion, while the dispersion of the SWNTs in the matrix still needs to improve in order to get better properties.

Chapter 4 Synthesis of Triblock Copolymer

PCL-PI-PCL and PCL-PI-PCL/SWNT/EP Composites

4.1 Introduction

Polyimides are high-performance aromatic materials with interesting properties such as high glass transition temperature, strong interaction with 1D/2D carbon nanomaterials.¹⁰⁴ We have previously shown that polyimide (PI) is a very good dispersing agent for carbon nanotubes because of its strong π - π interaction with SWNT side wall.^{15, 16} However, PI is only soluble in polar aprotic solvents such as DMSO, NMP and DMF. Its poor solubility and incompatibility with common organic solvents such as tetrahydrofuran THF, chloroform and acetone limits its applications. It would be desirable to modify PI in order to make it more soluble in common solvents. The sequential copolymerization of block copolymers of polyester-polyimide-polyester (PEs-PI-PEs) has not been reported. Ju *et al* synthesized polycaprolactone-*b*-polyimide-*b*-polycaprolactone (PCL-PI-PCL) triblock, for use as a dielectric material, via “grafting to” of PCL-furyl amine to maleimide-PI.¹⁰⁵ However, the “grafting to” method may be somewhat limited by efficiency and solvent compatibility of the two blocks. They linked PCL and PI by Diels-Alder reaction, which is reversible, so the triblock may decompose with heating.¹⁰⁵ Other polyimide-vinyl block copolymers were synthesized via atom transfer radical polymerization (ATRP)¹⁰⁶; which include polyimide-graft-polystyrene¹⁰⁷ and poly(methyl methacrylate)-polyimide-poly(methyl methacrylate)¹⁸. Polyimide-polyester block copolymers have hitherto not been reported.

Ring-opening polymerization has not employed previously for the synthesis of PI-based copolymers.

Single wall carbon nanotubes (SWNTs) are high-performance nano-materials being exploited for diverse applications such as polymer matrix composites, antibacterial nanomaterials¹⁰⁸, field-effect transistors^{109, 110}, biosensors^{111, 112}, *etc.* Their intrinsic mechanical, electrical and optical properties are outstanding.¹ However, realization of these properties in practice typically depends on achieving good dispersion of SWNTs in common solvents such as tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile, *etc.* The high surface area of nanotubes results in strong inter-tube van der Waals forces² so that they easily aggregate to form bundles. Nanotube dispersing agent ought to have strong affinity to nanotubes as well as good solubility in common solvents, which may entail contrasting compositional requirements for the dispersing agent. Both covalent and noncovalent functionalization approaches have been reported.²⁻⁴ Covalent functionalizations can improve dispersion but typically destroy the long-range π conjugation of SWNTs.⁵ Noncovalent functionalizations usually do not disrupt the intrinsic structure of SWNTs, but the types of polymers and organic solvents that can be applied are still limited.^{6, 7} Recently, conjugated and aromatic polymers/copolymers have attracted much attention as dispersing agents.^{8, 113, 114} PI-BDA is an effective dispersant as reported by Yuan Wei, but it is insoluble in low boiling point solvents, which makes the fabrication temperature higher for removing the high boiling point solvent.

In this chapter, we synthesized a triblock copolymer using PI as centre block and polycaprolactone (PCL) as side blocks via a novel synthesis route. The ABA block copolymer was synthesized through addition of hydroxyl (-OH) active groups at the two ends of centre PI block as a macro initiator, followed by ring-opening

polymerization of the PCL end blocks.^{17, 18} The centre PI block noncovalently adheres to carbon nanotubes and the two end PCL blocks provide good solubility in THF solvent (a model solvent). The polymers were characterized with NMR, GPC and FT-IR spectroscopy. SWNT dispersions, using PCL-PI-PCL and PI alone, were characterized with UV-VIS-NIR, AFM, TEM, and Raman spectroscopy.

4.2 Experimental section

4.2.1 Materials

SWNTs (brand name as P2-SWNTs) (purity = 90%, diameter 4-5 nm, length 0.5-1.5 μ m) were obtained from Carbon Solutions, Inc. Polycaprolactone (average Mw~14,000 and average Mn~10,000) as control was purchased from Sigma-Aldrich. 3,3'-Dihydroxy-4,4'-diaminobiphenyl (HAB, 97%) was obtained from Tokyo Chemical Industry and purified by recrystallization from N,N'-dimethylformamide (DMF)/water mixture. 4-aminophenethyl (APA) was purified by recrystallization from ethanol. 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane anhydride (BPADA) was purified by recrystallization after dissolving in acetic anhydride and toluene and refluxed. N-Methyl-2-pyrrolidone (NMP), *m*-xylene and ϵ -caprolactone (CL) were dried with calcium hydride and distilled before use. Other chemicals were used without further purification.

4.2.2 Synthesis of α , ω -dihydroxy- polyimide macroinitiator (OH-PI-OH)

Under nitrogen flow, HAB (1.62 g, 7.50 mmol) and APA (0.69 g, 5.00 mmol) were dissolved in 15 mL of NMP with continuous stirring for 30 min. Subsequently,

BPADA (5.18 g, 10 mmol) was added into the solution. The reaction mixture was stirred at 25°C for 10 h, and then 10 mL of *m*-xylene was added into the poly (amic acid) solution. The solution was then refluxed at 180°C for 6 h to achieve thermal imidization (Scheme 4.1). The viscous product was slowly poured into a large amount of ethanol (volume ratio = 1:10), and the resulting precipitate was subsequently filtered. The OH-PI-OH product was dried at 70°C for 24 h under reduced pressure. The molecular weight of synthesized OH-PI-OH is 12100 g/mol and PDI is 1.42. ¹H NMR (300 M, *d*₆-DMSO, 25°C): δ 10.31 (s, Ar-OH), 7.88-8.04 (m, Ar-*H*), 7.40-7.21 (m, Ar-*H*), 7.21-7.02 (m, Ar-*H*), 4.76 (s, -CH₂-OH), 3.50 (tr, -CH₂-CH₂-), 2.77 (tr, -CH₂-CH₂-), 1.70 (s, -CH₃). (**Figure 4.1**)

Scheme 4.1 Synthesis of PCL-PI-PCL triblock copolymer: (a) dry NMP, 25°C, 10 h; (b) dry *p*-xylene, reflux, 6 h; (c) Sn(Oct)₂, dry NMP, 25°C, 6 h (d) CL, 100°C, 24 h.

4.2.3 One-pot synthesis of triblock copolymer of PCL-PI-PCL

In a glove box, OH-PI-OH (0.8 g, 0.1 mmol) (M_n = 12100 g/mol and PDI 1.42) was first dissolved in 1 mL NMP, after which Sn(Oct)₂ (0.081 g, 0.2 mmol) in toluene

was added into the solution. The mixture was kept stirring for 6 h. Freshly distilled CL (1.14 g, 10 mmol) was added into the mixture using a syringe. A highly viscous solution formed after 4 h and the polymerization was continued at 100°C for another 24 h. The crude product was poured into excess ethanol and the pale yellow precipitate was filtered. To obtain pure triblock copolymer, the precipitate was repeatedly dissolved in NMP and precipitated in methanol for 2 more times followed by drying overnight at 70°C for 24 h under reduced pressure.

Figure 4.1 ¹H NMR of (a) PCL (CDCl₃, 25°C), (b) OH-PI-OH (d₆-DSMO, 25°C) and (c) PCL-PI-PCL (d₆-DSMO, 25°C) (* : NMP residue).

4.2.4 Dispersion of SWNTs with various dispersing agents in DMF and THF

The concentration of SWNTs in solution can be estimated from the Beer-Lambert law, demonstrated in Page 53 of this thesis. The absorbance of very dilute polymer solutions (0.001, 0.002, 0.003 and 0.01 mg/mL in THF with dispersing agent PI, prepared by tip sonication for 30 min (1 and 1 second on/off)) was measured and the

absorbance at 500 nm was plotted against SWNTs concentrations. The extinction coefficient is the slope of the absorbance/SWNT concentration relation.

A 0.1 mg/mL solution of PCL-PI-PCL/SWNTs (mass ratio 1:1) in THF was prepared by tip sonication for 30 min (1 and 1 second on/off) and the absorption at 500 nm was measured immediately after centrifugation at 6000 rpm for 10 min and 10000 rpm for 10 min. Control measurements were made of SWNTs and OH-PI-OH/SWNTs in THF with the same concentration and centrifuge preparation.

4.2.5 Fabrication of PCL-PI-PCL/epoxy/SWNT films

Epoxy films reinforced with SWNTs were fabricated by solution casting method. L20 epoxy part A and B were mixed and pre-cured at 40°C for 30 mins. The dispersed PCL-PI-PCL/SWNT (1 mg/mL, 2 mg/mL, etc.) in THF were prepared via tip sonication (150 W, 60%) for 15 mins and then added to the calculated amount of pre-cured epoxy. After thoroughly mixing by bath sonication, the solution was cast on glass plate. After evaporating the solvent, the films were fully dried in vacuum oven at 40°C. The films were then peeled off from the glass and cured at 130°C for 3 h.

4.2.6 Structure analysis and characterization

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) carried out with a Shimadzu LC-20A Series GPC system equipped with a pump, a BC-PL gel mixed column, and a RID-10A refractive index detector, using DMF with 0.02M LiBr as the eluent and polystyrene standards as reference. Raman characterization was performed on a Renishaw Raman scope with HeNe laser at 785 nm excitation wavelength, recorded on dried droplets of undiluted dispersions. The dispersions were filtered through a PTFE membrane and dried in

vacuum to remove the solvents. The absorption spectra of OH-PI-OH or PCL-PI-PCL-dispersed SWNTs dispersions were measured with a Varian Cary 5000 UV-vis-NIR spectrophotometer. ^1H NMR spectra were recorded at 25°C using a Bruker AVANCE-300 (300 MHz) spectrometer with CDCl_3 or dimethylsulfoxide as solvents and TMS as internal reference. Infrared (IR) spectra were recorded with a Perkin Elmer Spectrum One at 4.0 cm^{-1} resolution. Atomic force microscopy (AFM) was conducted using a MFP 3D microscope in ac mode; dilute SWNT/PCL-PI-PCL (mass ratio = 1:1) dispersion in THF was prepared via sonication and then deposited onto a clean silicon wafer and evaporated the solvent. High-resolution transmission electron microscopy (TEM) images were obtained using a JEOL Model 3010F analytical electron microscope operated at an accelerating voltage of 200 kV. TEM samples were prepared by placing several drops of SWNT/OH-PI-OH (mass ratio = 1:1) suspension or SWNT/PCL-PI-PCL (mass ratio = 1:1) dispersion in THF on a 200 mesh carbon-coated copper grid (Easylab) and drying at room temperature.

4.3 Results and discussion

4.3.1 Design and synthesis of OH-PI-OH macroinitiator and PCL-PI-PCL copolymer

The synthesis route of OH-PI-OH and PCL-PI-PCL is shown in Scheme 4.1. The OH-PI-OH macroinitiator was synthesized via a two-step reaction starting from BPADA, HAB and APA dissolved in NMP. During the first step, the three monomers underwent polycondensation at room temperature to form a yellow color viscous poly(amic acid) solution, while in the second step at 180°C, a dark brown polyimide was formed after thermal imidization. Two terminal OH groups of polyimide were

observed in **Figure 4.1(b)** ($\delta_{\text{OH}} = 4.76$ ppm, $\delta_{\text{CH}_2\text{-OH}} = 3.50$ ppm and $\delta_{\text{CH}_2\text{-CH}_2} = 2.77$ ppm).

The as-prepared OH-PI-OH can easily react with stannous octoate ($\text{Sn}(\text{Oct})_2$) to yield an α,ω -Sn(Oct) terminated PI initiator, which can undergo ring-opening polymerization with cyclic ester monomers, such as ϵ -caprolactone, lactones and carbonates *etc.* The triblock copolymer PCL-PI-PCL was successfully synthesized and confirmed with FTIR and ^1H NMR (**Figure 4.1** and **Figure 4.2**). The chemical shifts at 4.00, 2.30, 1.56 and 1.32 ppm are assigned to the PCL block, compared to those of homopolymer (**Figure 4.1a, 4.1c**). The FTIR spectrum of the triblock copolymer has bands around $2800\text{--}3000\text{ cm}^{-1}$ (C–H stretching) which can be assigned to characteristic absorption bands of PCL components. Further, the characteristic bands of polyimide around 1730 cm^{-1} (C=O stretching), 1360 cm^{-1} (C–N stretching) and 1200 cm^{-1} (aromatic-OH stretching) were observed in both OH-PI-OH and PCL-PI-PCL. The broad peaks around $3400\text{--}3500\text{ cm}^{-1}$ can be attributed to O–H stretching (**Figure 4.2**).

Figure 4.3 shows the GPC curve of OH-PI-OH and PCL-PI-PCL. The molecular weight of PI was 12100 and that of PI-PCL-PI was 18600 with polydispersity index of 1.42. The M_n of the triblock copolymer exceeds that of the OH-PI-OH. The PDI remains narrow, indicating that the PCL-PI-PCL is a true triblock copolymer and not a mixture.

Figure 4.2 FT-IR spectra of PCL, PI and PCL-PI-PCL.

Figure 4.3 GPC curves of OH-PI-OH and PCL-PI-PCL running in 2 mg/mL DMF solution.

4.3.2 SWNTs dispersion and interfacial bonding with PCL-PI-PCL

SWNTs dispersion in THF using PCL-PI-PCL copolymer as the dispersing agent was quantitatively evaluated using UV-VIS-NIR absorption spectra and the Beer-Lambert law (see Experimental section). The absorbance at 500 nm was plotted against SWNTs concentrations (**Figure 4.4(a)**). A linear-least-squares fit to the data gives a slope of 21.6, which can be used for back-calculating the SWNTs concentration in other solutions (**Figure 4.4(b)**).

The nanotube concentrations of the supernatants of PCL-PI-PCL/SWNTs were evaluated immediately after sonication, or sonication followed by centrifugation at 6000 rpm or 10000 rpm each for 10 min. The supernatants of dispersions using the control polymer of OH-PI-OH/SWNTs under the various settling conditions were similarly evaluated and compared (**Figure 4.4b**). Immediately after sonication, both PCL-PI-PCL/SWNTs and OH-PI-OH/SWNTs dispersion had nearly the same nanotube concentration ~50 mg/L. After centrifugation, the nanotubes concentrations in the supernatants of PCL-PI-PCL/SWNTs decreased to 33 and 28 mg/L for 6000 rpm and 10,000 rpm respectively, which was much higher than that of OH-PI-OH/SWNTs (6 and 3 mg/L), suggesting that the dispersion of SWNTs in THF is greatly improved by incorporation PCL end blocks in the dispersant.

Figure 4.4 (a) Absorption spectra of SWNTs/polymer dispersant (mass ratio = 1:2) at different nanotube concentrations. Insert shows the absorbance of the dispersion at 500 nm. The straight line is a linear-least-square fit to the data. (b) SWNTs concentrations of OH-PI-OH dispersed and PCL-PI-PCL dispersed in THF under different conditions: immediately after sonication, after centrifugation at 6000 rpm for 10 min, and after centrifugation at 10 000 rpm for 10 min. Photographs of SWNTs dispersed in THF using OH-PI-OH (control, left) or PCL-PI-PCL (right) (c) immediately after sonication; and (d) after 1 h standing.

Figure 4.4(c-d) shows photographs of SWNTs dispersed in THF using OH-PI-OH (control) and PCL-PI-PCL as dispersing agents. After sonication, both of the solutions were black. However after standing for one hour, the SWNTs dispersed in OH-PI-OH

solution mostly settled, while no obvious aggregates were observed in the PCL-PI-PCL/SWNTs solution, indicating a homogeneous stable dispersion of SWNTs was achieved with the triblock polymer. This is mostly because the solubility of PI is very poor in THF while the solubility of PCL in THF is good. The solubilities of PCL, OH-PI-OH, and PCL-PI-PCL in different solvents are shown in **Table 4.1**.

To further examine the nanotube dispersion and morphology, TEM and AFM images of the dispersed SWNTs were obtained and shown in **Figure 4.5** and **Figure 4.6** respectively. The OH-PI-OH-dispersed SWNTs, which were used as the control, formed bundles with large diameters of about 30 nm (**Figure 4.5a**), while the majority of the PCL-PI-PCL-dispersed SWNTs were observed in smaller bundles of diameters of around 5 nm (**Figure 4.5b**). At lower magnification (**Figure 4.5c**), it can be seen that the carbon nanotubes are wrapped with PCL-PI-PCL polymer and also intercalated by the polymers, to which the superior dispersion and longer-term stability of the SWNTs solution may be attributed. The ability of the triblock copolymer to disperse SWNTs into smaller bundles and individual tubes is also observed by AFM imagery (**Figure 4.6**). As shown in **Figure 4.6**, most of the dispersed SWNTs had lengths of around 1 μm , indicating that noncovalent dispersant did not significantly reduce the nanotube length. The measured height of the SWNTs was below 5 nm, and some are 1~2 nm, suggesting that the SWNTs were dispersed as small bundles and individual tubes. Here we used lower sonication power (150W, 60% amplified tip-sonicator) to preserve the length of carbon nanotubes so not all tubes were debundled into individual tubes.

Figure 4.5 TEM images of dispersed SWNTs with (a) OH-PI-OH (control) (b) PCL-PI-PCL (c) PCL-PI-PCL (lower magnification). The dilute (0.01mg/mL) solution of SWNTs were dropped on copper grids a few times.

Figure 4.6 AFM image of PCL-PI-PCL-dispersed SWNTs deposited on silicon wafers by drop-casting the dilute (0.01 mg/mL) solution a few times.

Table 4.1 Solubility of PCL, OH-PI-OH and PCL-PI-PCL (1 mg polymer in 5 mL solvent).

Polymer	Solubility							
	NMP	DMF	THF	DCM	Toluene	Hexane	MeOH	water
PCL	+	+	+	+	+	+	-	-
OH-PI-OH	+	+	+	+	-	-	-	-
PCL-PI-PCL	+	+	-	-	-	-	-	-
+, good solubility; -, insoluble after 30 min								

To confirm the strong interaction between the synthesized polymer and carbon nanotubes, 785 nm laser Raman spectra of pure P2-SWNTs and different polymer-dispersed (PCL, OH-PI-OH and PCL-PI-PCL) P2-SWNTs were obtained in solution form and filtered through PTFE films. The spectra are shown in **Figure 4.7**. It is known that covalent functionalization can introduce defects into SWNTs, leading to increased intensity of the D-band ($\sim 1330 \text{ cm}^{-1}$).^{63, 115} With non-covalent functionalization by the various polymers (PCL, OH-PI-OH and PCL-PI-PCL), the intensity ratios of the D band to the G band (I_D/I_G) of the various dispersions are not larger than that of unfunctionalized P2-SWNTs (**Figure 4.7a**), corroborating that the nanotube graphene structure was well preserved. However, the G band showed varying degrees of shift. For PCL-PI-PCL, the G+ band shifted from 1592.53 cm^{-1} to 1589.63 cm^{-1} , indicating n-doping due to charge transfer from the polymer to SWNTs (**Figure 4.7a**).¹⁰¹ This means PCL doping is electron-giving due to the oxygen and alkyl chain on it. The Raman radial breathing mode (RBM) peaks also become broader due to the interaction between the polymer and SWNTs,¹¹⁶ and the change of the shape is more obvious in OH-PI-OH and PCL-PI-PCL dispersed carbon nanotubes (**Figure 4.7b**). The RBM is

related to the radius of carbon nanotubes, so the up-shift of RBM peaks (**Figure 4.7b**) are attributed to the polymer wrapping.¹¹⁷ This does not mean that Raman spectrum is not able to differentiate between the CNT and the polymer but rather due to pure polymer do not have Raman signals in the measured area.

Figure 4.7 Raman spectra of pure P2-SWNTs and polymer-dispersed SWNTs using 785 nm laser.

4.3.3 SWNTs dispersion in PCL-PI-PCL/epoxy films and the mechanical properties of the composite films

As PCL-PI-PCL can disperse SWNT well in THF solvent, we used it as the dispersant of nanotubes for epoxy composite fabrication with a range of SWNT loadings. Some typical PCL-PI-PCL/epoxy/SWNT composite films of different loadings are shown in **Figure 4.8**. The neat epoxy films or PCL-PI-PCL films are opaque and no black color. After adding SWNTs, the films become black. The dark films are homogeneous for all three loadings (2 wt%, 4 wt% and 6 wt%) of CNTs with no visible agglomeration. The mechanical properties of the films are summarized in **Table 4.2**. Among all the composite films, 2 wt% SWNTs loading achieved the best mechanical properties. Its

strength, modulus and elongation at maximum stress are 74%, 35% and 62%, respectively, higher than those of the PCL-PI-PCL/epoxy control film made with 0 wt% SWNTs. The modulus of the composite films increased when increasing the amount of carbon nanotubes. At the higher SWNT loading, the strength and elongation properties decreased. This may be due to the increase of free volume in the composite films brought by SWNTs.¹¹⁸

Table 4.1 Mechanical Properties of PCL-PI-PCL/SWNT/epoxy composite films

SWNT (wt%)	Strength (MPa)	Modulus (MPa)	Elongation at maximum
	(increase %)	(increase %)	stress (%)
0	35.3±6.6	1709.9±191.7	3.40±1.16
2	61.4±2.2 (74)	2307.0±136.3 (35)	5.50±1.04
4	48.5±3.2 (37)	2318.5±184.7 (36)	4.24±0.81
6	45.2±4.3 (28)	2431.1±107.6 (42)	3.46±0.48

Figure 4.8 Visual appearance of PCL-PI-PCL/epoxy/SWNT composite film (a) 2 wt% SWNTs (b) 4 wt% SWNTs (c) 6 wt% SWNTs.

Fracture surfaces of the composite films after tensile testing were shown in **Figure 4.9**. There were some pull-outs observed for the 2% SWNTs fractured surface but they were not too extensive. The SWNTs were well dispersed in the composite films and no obvious agglomeration was observed, indicating that the PCL-PI-PCL triblock was an effective SWNT dispersant for epoxy composites.

Figure 4.9 FE-SEM images of fracture surface of PCL-PI-PCL/epoxy/SWNT with 2 wt% SWNT loading at (a) low magnification ($\times 5000$) and (b) high magnification ($\times 20000$) and (c) neat epoxy matrix without CNT (control).

4.4 Conclusion

We have successfully synthesized the triblock copolymer polycaprolactone-polyimide-polycaprolactone (PCL-PI-PCL) via a 2-step sequential polymerization process of polycondensation followed by ring-opening polymerization. The PCL-PI-PCL copolymer disperses the SWNTs effectively in THF, even under high-speed centrifugation and standing. The PCL-PI-PCL dispersed SWNTs can be incorporated into epoxy composites. We showed that the PCL-PI-PCL triblock-dispersed SWNTs (2 wt%) led to 74%, 35% and 62% increase in the tensile strength, modulus and elongation of the nanotube/dispersant epoxy films compared to the control without nanotubes. The excellent nanotube dispersion properties of the copolymer were due to the combination of strong charge transfer between the nanotube and PI, as well as the good solubility of the PCL end blocks in the chosen solvent (THF).

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Chapter 5 Other Triblock Copolymer Dispersants with PI Center Blocks for SWNTs/EP Composites

5.1 Introduction

Block copolymers offer interesting properties since they typically possess properties of the different blocks. Polyimides (PI) are a class of widely used aromatic high-performance polymers due to their outstanding thermal, mechanical, physicochemical, and dielectric properties.¹²⁰⁻¹²⁵ PI has been widely used as reinforcing agents in polymer blends to improve their mechanical properties.¹²⁶⁻¹²⁸ However, the PI's poor solubility and incompatibility with common organic solvents due to their rigid chain characteristics has limited their applications. To improve the polyimide solvent compatibility whilst generally retaining the desired PI properties, copolymerization with another polar comonomer,¹²⁹ increasing the alkyl chain length^{130, 131} or adding sulfonated groups¹³² to the polyimide has been explored. Nagai *et al* has prepared ABA-type triblock copolymers of polymethylmethacrylate-*b*-polyimide-*b*-polymethylmethacrylate (PMMA-PI-PMMA) using difunctional fluorine-containing polyimide as atom-transfer radical polymerization (ATRP) macroinitiator for use as a porous interlayer insulation membrane in large-scale microelectronic integration.¹³³ Nagai *et al* also applied ATRP to initiate the polymerization of 2-methyl-2-adamantyl methacrylate (MAdMA) from the PI block, and the resulting triblock (PMAdMA-*b*-PI-*b*-PMAdMA) exhibited high hydrophobicity, high H₂/CO₂ selectivity and low dielectric constant.¹³⁴ Luo *et al* prepared poly(ethylene oxide) (PEO)-containing segmented copolymers from polyetheramine and pentaerythritol-based polyimide for highly CO₂-

selective gas separation.¹³⁵ Fischer *et al* synthesized polyimide-*b*-polydimethylsiloxane (PI-PDMS) block copolymers from amino-terminated polysiloxanes to develop flexible LEO(low earth orbit)-resistant PI films.¹³⁶ Thus, there has been great interest in increasing the solubility of PI-derived copolymers in common organic solvents as well as confer functionalizable groups to the copolymers to further exploit its outstanding properties.

The synthesis of block copolymers derived from PI and polylactide or functionalizable polycarbonate has not yet been reported. Also, PLA is non-functionalizable. The synthesis of poly(2-methyl-2-(allyloxycarbonyl)propylene carbonate) (PMAC) which is a type of poly(ester-carbonate) with pendant allyl group that allows post-functionalization has been reported.¹³⁷⁻¹³⁹ On the other hand, block copolymers of PMAC with PI has not been reported. We hypothesize that these block copolymers may act as effective dispersants of single-walled carbon nanotubes (SWNTs) since the PI has good π - π interaction with SWNTs while the PLA/PMAC block has good solubility in low boiling point solvents such as tetrahydrofuran (THF), chloroform (CHCl₃) and dichloromethane (CHCl₂).

This chapter reports our design and synthesis of 3 series of novel triblock (TB) copolymers (Scheme 5.1) of (i) polylactide-*b*-polyimide-*b*-polylactide (PLA-PI-PLA) (labeled as TB1a and TB1b with different PLA chain lengths, **Table 5.1**); (ii) PMAC-PI-PMAC (labeled as TB2a and TB2b, **Table 5.1**), and (iii) epoxidized (EP) derivative of PMAC-PI-PMAC (hereafter referred to as PMACEP-PI-PMACEP) (labeled as TB3a and TB3b, **Table 5.2**). The triblock copolymers are synthesized through addition of hydroxyl (-OH) groups at polyimide terminals, followed by ring-opening polymerization of lactide and functional carbonate (Scheme 5.1). The copolymers are used as dispersing agents of single walled carbon nanotubes (SWNTs) in THF and then

the TB-dispersed SWNTs in THF are mixed with epoxy resin to make nanocomposite films. In order to confer reactivity of the TB copolymer dispersing agent with the epoxy resin matrix for improving the transfer of stress from SWNTs to the resin, the vinyl groups of PMAC-PI-PMAC copolymers are epoxidized with 3-chloroperbenzoic acid (*m*-CPBA) to obtain pendant epoxy-containing copolymers (TB3a and TB3b, Scheme 1). The copolymers were characterized by NMR, FTIR and GPC. The SWNT dispersion in THF was examined by UV-VIS-NIR and Raman spectroscopy, and SWNT/matrix interaction were examined by FE-SEM and TEM. It was found that TB1b, TB2b and TB3b triblock copolymers could effectively disperse SWNTs. The polyimide block non-covalently interacts with SWNTs while polyesters/polycarbonate (PLA/PMAC) provides good solubilities in low boiling point solvents (THF, CHCl₃ and CHCl₂) (**Table 5.3**). We also measured the tensile properties of the nanocomposite films. The optimized triblock copolymer (TB3b) dispersed SWNTs (2 wt%) increased the tensile strength, modulus, and elongation of the epoxy nanocomposites by 40%, 34%, and 26% respectively compared to neat epoxy.

Scheme 5.1 Synthesis of PLA-PI-PLA and PMAC-PI-PMAC triblock copolymers.

Table 5.1 Synthesized triblock copolymers initiated by different polyimide homopolymers.

Sample	Monomer	Design [I]:[M] ^a	Initiator (Mn (Da))	Mn (Da) /PDI ^b	Actual Ratios of n:m:n ^c
TB1a	<i>rac</i> -LA	1:50	PI (6900)	9780/1.55	10:10:10
TB1b	<i>rac</i> -LA	1:80	PI (6900)	15500/1.59	30:10:30
TB2a	MAC	1:80	PI (6900)	11000/1.78	10:10:10
TB2b	MAC	1:150	PI (6900)	15000/1.90	20:10:20

^a Mole ratio of polyimide macroinitiator and LA/MAC monomers for ring-opening polymerization.

^b Determined from GPC using polystyrene standards as references.

^c Calculated from the molecular weight of polymers and single units.

Table 5.2 Synthesized PMACEP-PI-PMACEP (TB3a, TB3b) from PMAC-PI-PMAC (TB2a, TB2b).

Sample	Design [m-CPBA]:[ene] ^a /Actual Ratios of alkene and epoxy	TB measured Mn (Da) ^b
TB3a	1:2/1:1	11100
TB3b	1:2/3:1	15300

^a Mole ratio of m-CPBA and alkene groups in TB2a and TB2b.

^b Determined from GPC using polystyrene standards as references.

Table 5.3 Solubility of TBs in the common solvents (1 mg TB in 5 mL solvent).

Polymer	solubility				
	NMP	DMF	THF	MeOH	water
TB1b	+	+	+	-	-
TB2b	+	+	+	-	-
TB3b	+	+	+	-	-
+, good solubility; -, insoluble after 30min					

5.2 Experimental section

5.2.1 Materials

P2-SWNTs (purity = 90%, diameter 4-5 nm, length 0.5-1.5 μm) were obtained from Carbon Solutions, Inc. They were purified via thermal oxidation at 400 °C for 2 h in air, followed by refluxing in 6 M HCl solution overnight. α,ω -dihydroxy-polyimide macroinitiator (OH-PI-OH) was synthesized according to the previous work.¹³ D,L-Lactide was purchased from Sigma-Aldrich and recrystallized in anhydrous EtOAc. 3-Chloroperbenzoic acid (*m*-CPBA), 2,2-Bis(hydroxymethyl) propionic acid, allyl bromide and tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) were purchased from Sigma-Aldrich. Epoxy resin (Part A: EPR L20 and Part B: EPH 960) was obtained from Bakelite. Dimethylacetamide (DMAc) and dimethylformamide (DMF) were dried with calcium hydride and distilled before use. Other chemicals were used without further purification.

5.2.2 Structure analysis and characterization

The molecular weights and molecular weight distributions of the synthesized copolymers were determined by gel permeation chromatography (GPC) with a Shimadzu LC-20A Series GPC system equipped with a pump, a BC-PL gel mixed

column, and a RID-10A refractive index detector, using DMF with 0.02 M LiBr as the eluent and polystyrene standards as reference. ^1H NMR spectra were recorded at 25 °C using a Bruker AVANCE-300 (300 MHz) spectrometer with CDCl_3 or d_6 -DMSO as solvents and TMS as internal reference. FTIR was recorded with a Perkin Elmer Spectrum One at 4.0 cm^{-1} resolution. The absorption spectra of TB-dispersed SWNTs dispersions were measured with a Varian Cary 5000 UV-vis-NIR spectrophotometer. Raman spectra were carried out on a Renishaw Raman scope with He-Ne laser at an excitation wavelength of 633 nm. The dispersions were prepared according to the previous report¹¹⁹ and then filtered through PTFE membrane and dried to remove the solvents for Raman characterization. High-resolution transmission electron microscopy (TEM) images were obtained using a JEOL Model 3010F analytical electron microscope operating at an accelerating voltage of 200 kV. TEM samples were prepared by placing several drops of TBs/SWNT (mass ratio of polymer and SWNTs = 2:1) suspension dispersion in THF on a 200 mesh carbon-coated copper grid (EasyLab) and dried. Tensile tests of composite films were performed on an Instron 5543 Tensile Meter with a 100 N load cell at room temperature. The crosshead speed was 2.5 mm/min. The dimensions of the compound are about 20 mm, 4 mm, and 60 μm (length, width and thickness). Mechanical properties of each composite formulation were measured on five to ten specimens, and property averages and standard deviations were computed. Field-emission scanning electron microscope (FE-SEM) images were acquired using a JEOL JSM-6700F microscope. The fractured surfaces of composite films were coated with a thin layer of gold prior to SEM observation.

5.2.3 Synthesis of monomer MAC

The cyclic carbonate monomer 2-methyl-2-(allyloxycarbonyl)propylene carbonate (MAC) was prepared according to the previous work.¹⁴⁰ The final products

were white crystals (yield: 50%). ^1H NMR (300 M, CDCl_3 , 25 $^\circ\text{C}$): δ [ppm] 5.91 (dd, 1H, $\text{CH}_2=\text{CH}-$), 5.30 (m, 2H, $\text{CH}_2=\text{CH}-$), 4.68 (d, 2H, $=\text{CH}-\text{CH}_2-\text{O}-$), 4.60 and 4.22 (d, 2H+2H, $-\text{C}-\text{CH}_2-\text{O}-$), 1.34 (s, 3H, $-\text{CH}_3$)(Figure 5.1).

Figure 5.1 ^1H NMR spectrum of MAC (CDCl_3 , 25 $^\circ\text{C}$).

5.2.3 One-pot synthesis of triblock copolymers PLA-PI-PLA and PMAC-PI-PMAC

In a glove box, OH-PI-OH (0.3 g, 50 μmol) ($M_n = 6900$ Da) was first dissolved in 2 mL DMAc, after which $\text{Sn}(\text{Oct})_2$ (74 mg, 60 μmol) in toluene was added into the solution. The mixture was stirred for 6 h. D,L-Lactide (0.36 g, 2.5 mmol for TB1a and 0.54 g, 4 mmol for TB1b) or MAC (0.80 g, 4 mmol for TB2a and 1.5 g, 7.5 mmol for TB2b) was added into the mixture at the room temperature. A highly viscous solution formed after 4 h and the polymerization was continued at 130 $^\circ\text{C}$ for another 24 h

(Scheme 5.1). The crude product was poured into excess ethanol and the pale yellow precipitate was filtered. To obtain pure triblock copolymers, the precipitates were dissolved in DMAc and precipitated in methanol twice followed by drying overnight at 70°C for 24 h under reduced pressure (yield = 75%). Other triblock copolymers with different molecular weights (**Table 5.1**) were synthesized via similar procedure.

5.2.4 Epoxidation of PMAC-PI-PMAC with *m*-CPBA

PMAC-PI-PMAC (TB3a) (0.11 g, 10 μ mol) was first dissolved in 5 mL CH₂Cl₂, and then 3-chloroperbenzoic acid (34.5 mg, 0.2 mmol) was added into the solution. The mixture was stirred for 12 h under the dark. The degree of epoxidation was determined by ¹H NMR. The crude product was poured into excess ethanol and the pale yellow precipitate was filtered. The precipitates were dissolved in DMF again and dialyzed for two days. The transparent solution was re-precipitated in the excess ethanol and the precipitate was dried overnight 70°C for 24 h under reduced pressure (yield = 70%). TB3b was synthesized via similar procedure.

5.2.5 Dispersion of SWNTs with various dispersing agents in THF

The actual concentration of SWNTs in solution can be estimated from the Beer-Lambert law, which we have demonstrated in our previous chapters. To determine the relation between SWNT concentration and the absorbance, the absorbance of certain concentrations of SWNTs solutions (0, 0.02, 0.04, and 0.1 mg/mL) in THF with dispersing agent TB1b, prepared by tip sonication for 15 mins (1 and 1 second on/off) was measured and the absorbance at 500 nm was plotted against SWNT concentrations.

We prepared 0.3 mg/mL TBs/SWNT (mass ratio 2:1) in THF and tip sonicated (150 W, 60%) for 15 min (1 and 1 second on/off), after which the absorption was

measured immediately. After centrifugation at 6000 rpm for 10 min and 10000 rpm for 10 min, the absorption values at 500 nm were also recorded.

5.2.6 Fabrication of TB/SWNT/epoxy Films

The composite films reinforced with SWNTs were fabricated by solution casting method. L20 epoxy part A and B were mixed and pre-cured at 40°C for 30 min. The dispersed TB/SWNT (1 mg/mL, 2 mg/mL, etc.) in THF were prepared via tip sonication (150 W, 60%) for 15 min and then added to the calculated amount of pre-cured epoxy. After thorough mixing by bath sonication, the solution was cast on PET film. The films were fully dried in vacuum oven at 40°C after evaporating the solvent. The films were then peeled off and cured at 130°C for 3 h.

5.3 Results and discussion

5.3.1 Design and Synthesis of PLA-PI-PLA PMAC-PI-PMAC and PMACEP-PI-PMACEP Copolymers

The α,ω -dihydroxy-polyimide macroinitiator (OH-PI-OH) was prepared according to our previous work.¹¹⁹ Briefly, the polyimide macroinitiator was synthesized from the condensation of a dianhydride (specifically 2,2-Bis[4-(3,4-dicarboxyphoxy)phenyl]]propane anhydride (BPADA)), diamine/amine (specifically 3,3'-Dihydroxy-4,4'-diamino-biphenyl (HAB) and 4-aminophenethyl alcohol (APA)) (molar ratio in feed [BPADA]/[HAB]/[APA] = 4:3:2). The ¹H NMR of OH-PI-OH is shown in **Figure 5.2** and the resonances at 10.17 ppm (labelled as 'a') are assigned to the hydroxyl protons of polyimide block; the resonance at 4.82 ppm (labelled as 'b') are attributed to the hydroxyl protons at the two ends. From the integration ratio of 'a' and 'b', we can get that the number of repeating units of the OH-PI-OH (indicated as

“m” in **Figure 5.2**) was around 4. The molecular weight (M_n) and molecular weight distribution (PDI) of the synthesized OH-PI-OH precursor are 6900 Da and 1.32, respectively. The OH-PI-OH precursor was then mixed with tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) to yield an α,ω -Sn(Oct) terminated PI macroinitiator, which can undergo further ring-opening polymerization with lactide (LA) and 2-methyl-2-(allyloxy-carbonyl)propylene carbonate (MAC). We have made two PLA-PI-PLA triblocks (labelled as TB1a and TB1b, Scheme 1) and two PMAC-PI-PMAC triblock copolymers (labelled as TB2a and TB2b, Scheme 5.1) with varying ratios of macroinitiator to monomer (**Table 5.1**). The PMAC-PI-PMAC polymer was also further epoxidized to produce PMACEP-PI-PMACEP (labelled as TB3a and TB3b, Scheme 5.1).

All the triblock copolymers were characterized by NMR and GPC. ^1H NMR spectrum of TB1a (and also of TB1b) have resonances at 7.17, 7.38, 7.97 and 10.14 ppm (**Figure 5.3** and **5.4**) which are assigned to the polyimide block, while the resonances centered at 1.41 (labeled as ‘e’) and 5.12 ppm (labeled as ‘b’) are attributed to the methyl and methyne protons of the PLA block. For TB2b (and also TB2a) (**Figure 5.5** and **5.6**), the resonances at 1.23 (labelled as ‘e’) and 5.94 ppm (labelled as ‘c’) are methyl and methylene protons of the PMAC block. After TB2a is epoxidized with 3-chloroperbenzoic acid, new signals at 2.34 and 2.71 ppm (labelled as ‘a’ and ‘c’, **Figure 5.7**) appear due to the protons of epoxy groups, and the ratios of the areas of ‘f’ and ‘a’ are approximately 1:1, indicating that approximately half of vinyl groups have been converted to epoxy groups (**Figure 5.7**). **Figure 5.8** shows the NMR spectrum of TB3b which was partially epoxidized from TB2b. The ratio of ‘f’ and ‘a’ is about 3:1, indicating the ratio of vinyl groups and epoxy groups is about 3:1.

The FTIR spectra of the OH-PI-OH and the synthesized triblock copolymers (TB1b, TB2b, and TB3b) are shown in **Figure 5.9a** and **5.9b**. The signals around 1700 cm^{-1}

(C=O stretching) and 1400 cm^{-1} (C–N stretching) are attributed to the imide groups on OH-PI-OH backbone (**Figure 2a**). The FTIR spectra of the triblock copolymers (**Figure 5.9b**) showed bands at around 2950 cm^{-1} (C–H stretching) and 1720 cm^{-1} (C=O stretching) which can be assigned to characteristic absorption bands of PLA and PMAC components. The peaks around 980 cm^{-1} can be attributed to the double bonds (–CH=CH₂) on MAC components. Further, the characteristic bands of polyimide around 1750 cm^{-1} (C=O stretching) and 1380 cm^{-1} (C–N stretching) are also observed in all copolymers (**Figure 5.9b**).

The M_n and PDI values of the triblock copolymers are also determined by GPC. **Figure 5.10** shows the GPC curves of the triblock copolymers (TB1a, TB1b, TB2a, TB2b, TB3a and TB3b) and also the homopolymer OH-PI-OH before copolymerization. The molecular weights of all the triblock copolymers increased as compared to that of the polyimide macroinitiator. The molecular weights of TB1a, TB1b, TB2a and TB2b are 9780, 15500, 11000 and 15000 Da, respectively, and PDIs are generally in the range of 1.55 to 1.90 (**Table 5.1**).

Figure 5.2 ¹H NMR spectrum of OH-PI-OH (d₆-DSMO, 25°C).

Figure 5.3 ¹H NMR spectrum of TB1a (d₆-DSMO, 25°C) (*: DMAC residue).

Figure 5.4 ^1H NMR spectrum of TB1b (d_6 -DSMO, 25°C) (*: DMAc residue).

Figure 5.5 ^1H NMR spectrum of TB2b (d_6 -DSMO, 25°C).

Figure 5.6 ^1H NMR spectrum of TB2a (d_6 -DSMO, 25°C).

Figure 5.7 ^1H NMR spectrum of TB3a (d_6 -DSMO, 25°C).

Figure 5.8 ^1H NMR spectrum of TB3b (d_6 -DSMO, 25°C).

Figure 5.9 FTIR spectra of (a) macroinitiator OH-PI-OH and (b) TBs.

Figure 5.10 GPC curves of OH-PI-OH, PLA-PI-PLA (TB1a, TB1b), PMAC-PI-PMAC (TB2a, TB2b) and PMACEP-PI-PMACEP (TB3a, TB3b).

5.3.2 SWNTs Dispersion and Interfacial Bonding with Triblock Copolymers

The dispersion of SWNTs in THF was evaluated by UV-Vis-NIR spectra. A series of concentrations of SWNTs were prepared (0, 0.02, 0.04, 0.1 mg/mL) and their absorbance at 500 nm were collected and plotted. A linear square fit to the data gives a slope of 23.2, which we then used to back-calculate the actual concentration of SWNTs according to Beer's law (**Figure 5.11a**). The actual concentrations of SWNTs dispersed by different TBs under different conditions are shown in **Figure 5.11b**. Immediately after sonication, the concentrations are around 0.3 mg/mL. After centrifugation at 6000

rpm and 10000 rpm for 10 min, the concentrations decrease as some of the SWNTs settled down, especially for the TB3a solution. In TB2b and TB3b, the concentrations maintain a relatively high value; for TB2b, the supernatant is at 0.11 mg/mL and 0.09 mg/mL after centrifugation at 6000 rpm (3743 RCF) and 10000 rpm (10397 RCF) respectively; for TB3b, the supernatant is at 0.10 mg/mL and 0.07 mg/mL at 6000 rpm and 10000 rpm respectively, indicating that TB2b and TB3b are fairly good dispersants. Comparing the same kind of copolymer with different molecular weights (TB2a verses TB2b, and TB3a verses TB3b respectively), a longer length of the end blocks can produce the best dispersion. For example, the CNT concentration of TB2a (0.08 mg/mL and 0.04 mg/mL at 6000 rpm and 10000 rpm respectively) with short chains is much lower than that of TB2b with longer chains (0.11 mg/mL and 0.09 mg/mL at 6000 rpm and 10000 rpm respectively) at both 6000 rpm and 10000 rpm. If the end blocks are shorter (like TB2a and TB3a), the dispersion appears to be unstable with higher speed centrifugation. Increasing the length of the end blocks will help to stabilize the dispersed SWNTs in THF because of their good solubility in the chosen solvent (THF). (However, the TB1a and TB1b seem to be quite similar in their dispersibility at 10000 rpm and this may be due to the better solubility of the PLA.) **Figure 5.12** shows pictures of dispersed SWNTs in different TB solutions corroborating the UV-VIS measurements. Immediately after sonication, all the solutions are black. After high-speed centrifugation, some SWNTs settled, especially in TB3a where the remaining SWNTs in the solution is very little, which corroborates with the results in **Figure 5.11b**.

Figure 5.11 (a) Absorption spectra of SWNTs/TB1b dispersant (mass ratio = 1:2) at different nanotube concentrations. Inset shows the absorbance of the dispersion at 500 nm. The straight line is a linear-least-square fit to the data. (b) SWNTs concentrations of TBs dispersed in THF under different conditions: immediately after sonication, after centrifugation at 6000 rpm for 10 min, and after centrifugation at 10 000 rpm for 10 min.

Figure 5.12 Photographs of SWNTs dispersed in THF using different TBs (a) immediately after sonication; and (b) and after centrifugation at 10000 rpm for 10 min.

In order to further evaluate the dispersing agents, the morphology of SWNTs dispersed by TB1b, TB2b and TB3b in THF were characterized by TEM (**Figure 5.13**). From the TEM pictures, all three copolymers can disperse SWNTs well and no obvious agglomeration were observed. The polymers also can be seen to be wrapped around the carbon nanotube surface and in between the nanotubes.

The Raman spectra of pristine SWNTs and copolymer-dispersed SWNTs are shown in **Figure 5.14**. The peaks around 1326 cm^{-1} and 1590 cm^{-1} correspond to the defects induced modes (D band) and G band, respectively. I_D/I_G ratios of the copolymer-dispersed SWNTs are comparable with that of pristine SWNTs indicating that there are no defects introduced into SWNTs (**Table 5.4**). The RBM peaks of the polymer-dispersed SWNTs ($156.7\text{ cm}^{-1}/173.8\text{ cm}^{-1}$) are upshifted by $\sim 7\text{--}9\text{ cm}^{-1}$ from the RBM peaks of pristine SWNTs ($149.3\text{ cm}^{-1}/164.8\text{ cm}^{-1}$). The G bands of the polymer-doped SWNTs (1592.0 cm^{-1}) is upshifted by around 1.1 cm^{-1} from the G band of pristine

SWNTs (1590.9 cm^{-1}). The 2D Raman band of pristine SWNTs is at 2628.8 cm^{-1} , while those of the TB-dispersed SWNTs are upshifted to 2634.9 cm^{-1} to 2638.3 cm^{-1} (**Table 5.4**). The upshift of G bands and 2D bands of the polymer-dispersed SWNTs is due to the π - π interaction between triblock copolymers and SWNTs. The noncovalent attachment doesn't alter the structure of SWNTs but the strong π - π interaction between wrapped polymer chains and the nanotubes are relatively strong to lead to the upshift.^{27, 141} Also, the RBM peaks are generally broadened due to the interaction between SWNTs and the dispersants.

Figure 5.13 TEM images of dispersed SWNTs with (a) TB1b (b) TB2b (c) TB3b at different magnifications.

Figure 5.14 Raman spectra of pristine SWNTs and polymer-dispersed SWNTs using 633 nm laser.

Table 5.1 Raman data of pristine SWNTs and TB/SWNTs.

Sample	I _D intensity	I _G intensity	I _D /I _G	RBM peaks (cm ⁻¹)	G band peaks (cm ⁻¹)	2D band peaks (cm ⁻¹)
SWNTs	2039.1	29159.3	0.070	149.3/164.8	1590.9	2628.8
TB1a/SWNTs	2439.2	57245.7	0.043	156.7/173.8	1592.0	2637.5
TB1b/SWNTs	3638.4	76024.1	0.048	156.7/173.8	1592.0	2636.6
TB2a/SWNTs	2732.5	55557.4	0.049	156.7/173.8	1592.0	2635.8
TB2b/SWNTs	3080.5	59194.3	0.052	156.7/173.8	1592.0	2634.9
TB3a/SWNTs	2402.2	59394.9	0.040	156.7/173.8	1592.0	2638.4
TB3b/SWNTs	2957.8	58997.1	0.050	156.7/173.8	1592.0	2636.6

5.3.3 SWNTs dispersion in TB/epoxy films and their mechanical properties

SWNTs (1 mg/mL or 2 mg/mL) are sonicated in the polymer/THF solvent (polymer concentration is 1 mg/mL) and the SWNT/polymer dispersion in THF is then added to the pre-cured epoxy mixture. After thorough mixing by bath sonication, the solution was cast and the solvent evaporated at room temperature. The films were then transferred to a vacuum oven and fully dried at 40°C for 24 h. After peeling off, the films were cured at 130°C for 3 h. The appearance of the composite films is shown in **Figure 5.15**. With addition of 0.5 wt% to 2 wt% SWNTs based on epoxy resin, all the SWNTs dispersed by the three polymers (TB1b, TB2b and TB3b) when mixed with

epoxy can produce homogenous films. No obvious agglomeration was shown in the pictures. In order to observe the dispersion more clearly, we also examined the fracture surface of the epoxy composites under FE-SEM and the images are shown in **Figure 5.16**. For all three different polymer dispersants, the SWNTs are well dispersed in the matrix and no agglomerations were observed with 0.5 wt% SWNT loading (**Figure 5.16b to 5.16d**). However, the SWNTs/epoxy film without TB shows some bundles and agglomeration (**Figure 5.16a**), indicating that the SWNTs are not evenly dispersed in the epoxy resin.

Further, we tested the mechanical properties (strength, modulus and elongation) of the neat epoxy and some composite films (see **Table 5.5**). Typical stress-strain curves are shown in **Figure 5.17**. From the tensile testing data, we can see that the TB(2 wt%)/EP blends (samples #2-4, **Table 5.5**) didn't show a decrease in their tensile properties compared to the neat EP resin, indicating good compatibility between the TB dispersant and the epoxy resin. From the tensile strengths, it appears that TB1b and TB3b have fairly good compatibility with the epoxy resin while TB2b, a polycarbonate with pendant allyl group, has poorer compatibility. This is reasonable since PLA is more polar than PMAC and so TB1b has better compatibility than TB2b, but the presence of epoxy group allows TB3b to covalently react with epoxy so that TB3b also shows better compatibility than TB2b.

When SWNT loading is 1 wt% (samples #5-7, **Table 5.5**), all the three SWNTs/TB/epoxy films show better tensile properties than the neat epoxy (sample #1, **Table 5.5**) and it is also true with the epoxy resin/TB blends (samples #2-4, **Table 5.5**). Amongst the samples 5-7 with 1 wt% SWNTs, TB1b (sample #5) has better tensile strength than the other 2 composites (samples #6 and #7). However, when the SWNT loading increased to 2 wt%, the tensile properties of SWNTs with TB1b and TB2b

(samples #8 and #9, **Table 5.5**) dropped compared to similar compositions made with 1 wt% SWNT loadings (samples #5 and #6, **Table 5.5**). As more SWNTs (2 wt%) are added, the properties for TB1b and TB2b (samples #8 and #9, **Table 5.5**) deteriorates possibly because of nanotube bundling and/or relatively weak nanotube/matrix interfacial bonding for the non-covalently functionalized SWNTs. With an increase in SWNT concentration, more macroscopic voids and more free volume may be introduced by SWNTs so that the mechanical properties of the composite films are affected.¹¹⁸ Some works even reported that the tensile properties start to decrease when SWNT loading is higher than 0.5 wt%.¹⁴²

Figure 5.15 Visual appearance of TB/epoxy/SWNT composite films (a) 0.5 wt% SWNTs (b) 1 wt% SWNTs (c) 2 wt% SWNTs (d) 0 wt% SWNTs (the controls) and (i) TB1b (ii) TB2b (iii) TB3b.

Figure 5.16 FE-SEM images of fracture surface of (a) SWNT/TB1b/epoxy (b) SWNT/TB2b/epoxy (c) SWNT/TB3b/epoxy with 0.5 wt % SWNTs loading in different magnifications (x10000, x20000, and x30000).

Table 5.1 Mechanical Properties of neat EP and SWNT/TB/EP Composite Films.
(The weight ratio of TB and SWNTs in the composites is 1:1.)

No.	sample	Strength (MPa)	Modulus (MPa)	Elongation at maximum stress (%)
1	neat EP	47.8±4.2	1933±176	4.19±0.75
2	TB1b(2 wt %)/EP	53.5±7.4	2453±363	3.31±0.81
3	TB2b(2 wt %)/EP	45.1±4.4	2273±349	2.84±0.29
4	TB3b(2 wt %)/EP	50.1±5.4	2316±176	3.26±0.45
5	SWNTs(1 wt %)/TB1b/EP	63.3±4.1	2577±371	4.79±0.80
6	SWNTs(1 wt %)/TB2b/EP	61.2±5.5	2112±169	5.16±0.46
7	SWNTs(1 wt %)/TB3b/EP	60.3±2.2	2108±312	5.82±1.12
8	SWNTs(2 wt %)/TB1b/EP	13.6±1.7	479±86	4.78±1.66
9	SWNTs(2 wt %)/TB2b/EP	55.1±4.4	2166±280	5.29±1.45
10	SWNTs(2 wt %)/TB3b/EP	66.9±2.8	2589±437	5.26±1.08

Interesting, with addition of epoxy functionalization in TB3b, the tensile properties with 2 wt% SWNTs (sample #10, **Table 5.1**) further improved compared with 1 wt% SWNTs (sample #7, **Table 5.1**). Among all those composite films, the SWNTs (2 wt%)/TB3b/EP (sample #10, **Table 5.1**) shows the best properties. Its tensile strength is 66.9±2.8 MPa, which is a 40% increase compared to the neat epoxy (47.8±4.2 MPa);

its modulus reaches 2589 ± 437 MPa, which is a 34% increase compared to the neat resin (1933 ± 176 MPa) and its elongation increased by 26%.

We and others have investigated SWNT dispersion for diverse applications such as nanoelectronics,^{109, 143} polymer matrix composites,^{127,130} antibacterial agents,¹⁴⁴ biosensors *etc.*,^{111,112} because of their excellent optical, electrical, and mechanical properties. However, a key challenge in using SWNTs is their poor dispersibility and strong tendency to bundle because of the ultra-high surface area. Non-covalent, as opposed to covalent approach, can effectively disperse the SWNTs whilst preserving the integrity of the nanotubes.^{145, 146} The π - π interaction with carbon nanotubes has been exploited for dispersing SWNTs as reinforcing fillers using conjugated polymers or aromatic and hetero-aromatic polymers, such as polyfluorenes,¹⁴⁷ polybenzimidazole (PBI),⁸⁰ and polyimide.⁴

With high-strength composites, the typical matrix resins include epoxy, polyimide, vinyl ester, etc. They are usually soluble in organic solvents, but low-boiling point organic solvents are much preferred in their processing for ease of removal as residual solvents will result in voids. Our group has previously reported a graft polymer, polyimide-*graft*-bisphenol A diglyceryl acrylate (PI-BDA), which has been shown to be more effective in dispersing SWNTs into individual nanotubes or small bundles as compared to the pure polyimide without grafting.^{4, 16} The polyimide-*graft*-bisphenol A diglyceryl acrylate (PI-BDA) significantly improves the dispersion of SWNTs in the solvent but the latter is limited to dimethylformamide (DMF) solvent, a high boiling point solvent. In Chapter 4, we introduced the one-pot synthesis of polycaprolactone-*block*-polyimide-*block*-polycaprolactone (PCL-PI-PCL) triblock copolymers which improve the dispersion of carbon nanotube in THF. However, the incorporation of the

PCL-PI-PCL decrease the mechanical properties of the resulting blended matrix as the compatibility of PCL with epoxy is inadequate.

We are the first to report the successful synthesis of PLA-PI-PLA and polycarbonate -PI-polycarbonate block copolymers here. Reports on the copolymers of PI and polyester or polycarbonates are limited.^{148, 149} Polylactide (PLA) is known to be more polar than polycaprolactone (PCL). We have made 3 new PI-derived block copolymer dispersants here that can disperse SWNTs in low boiling THF. Further, our new TB3b is the best dispersant among the 3 copolymers for the SWNT/epoxy nanocomposites. It appears that TB3b has good interaction with SWNTs and also good reactivity with the epoxy resin; the covalent bonding between the TB3b dispersant and the epoxy resin allows better transfer of the force from the nanofillers to the resin matrix.

Figure 5.17 Typical Stress-Strain Curves of TBs/epoxy/SWNT composite films.

5.4 Conclusion

In summary, novel triblock copolymers of polylactide-*b*-polyimide-*b*-polylactide (TB1) and poly(2-methyl-2-(allyloxycarbonyl)propylenecarbonate)-*b*-polyimide-*b*-poly(2-methyl-2-(allyl-oxycarbonyl)-propylene carbonate) (TB2) and the epoxidized derivative (TB3) have been successfully synthesized. These three block copolymers improve the dispersion of SWNTs in THF, a low boiling solvent, compared with SWNTs dispersion without adding any block copolymer. With the epoxidized TB3, the tensile properties continue to increase even when the SWNTs content increases to 2 wt%. The tensile strength, modulus, and elongation of SWNTs (2 wt%)/TB3b/EP increases by 40%, 34% and 26% compared to the neat epoxy resin. This is the first report of a dispersing agent that works well in dispersing the SWNTs in a low boiling point organic solvent (THF) which has shown a significant increase in the mechanical properties of the SWNT-filled composite films. By introducing the alkene groups on the end blocks, we showed that triblock copolymers could be further functionalized to have chemical reactivity with the epoxy resin matrix. That's why TB3 dispersed SWNTs reinforcement can achieve the best mechanical properties among the three triblock copolymers.

Chapter 6 Conclusions and Recommendations

6.1 Conclusions

The difficulties associated with increasing the CNT content, uniformly dispersing CNTs, and improving CNT/matrix interfacial bonding are major obstacles in the development of CNT/polymer composites and their applications in industries. In this thesis, we developed a series of polymers for solubilizing CNTs in polymer matrices and improving the nanotube/matrix interfacial adhesion for reinforcement of composites. The chromium complexation method improve the tensile modulus of the composite possibly by increasing the adhesive bonding between the polymer and CNTs. The triblock copolymers can provide good solubility and stabilization of CNT solution, even in low boiling point solvents. By attaching epoxy functional groups to the PMACEP-PI-PMACEP triblock copolymer dispersant, the compatibility with the matrix will increase and the tensile properties of 2 wt % SWNT/Epoxy composite can be improved compared to the pristine epoxy.

In spite of their superlative properties, CNTs have not been demonstrated to achieve the expected level of reinforcement in polymer composites. This has been attributed to the shortcomings of the chemical modification of the CNTs, which is inevitable to disperse them in the polymer matrix. Hence, a novel approach to CNT-polymer composites with enhanced tensile modulus has been developed. This novel non-destructive route differs radically from the overwhelmingly popular CNT modification routes based on treatment with strong oxidizing acids (such as sulfuric and nitric), which cause serious damage to the CNT structure, including rupturing and length-shortening, which, in turn, compromise the CNTs' excellent mechanical properties, and have been blamed for the consequent below par performance of CNT-

composites. Synthesis of CNT-chromium complexes tailored for interaction with polymer matrices has been completed via organometallic dispersant. We have shown these novel complexes to have higher dispersibility in common organic solvents compared to the pristine CNTs, which may translate into more synergistic interaction in polymer matrices.

In addition, a novel triblock copolymer PCL-PI-PCL was synthesized via a two-step sequential polymerization process of polycondensation followed by ring-opening polymerization. This approach to triblock copolymer synthesis is versatile and efficient. Among many potential applications, effective SWNT dispersants can be applied to SWNT/epoxy composites to improve their mechanical properties. We show that the PCL-PI-PCL triblock-dispersed SWNTs (2 wt%) led to 74%, 35% and 62% increases in the tensile strength, modulus and elongation of the nanotube/dispersant epoxy films compared to the control without nanotubes. Our triblock copolymers avoided the use of high-boiling-point solvents such as DMF for dispersing CNTs because of the good solubility of PCL blocks. The excellent nanotube dispersion properties of the copolymer were due to the combination of strong charge transfer between the nanotube and PI, as well as the good solubility of the PCL end blocks in the chosen solvent (THF). The replacement of caprolactone with other monomers may provide a route to the synthesis of highly effective SWNT dispersants in a wide range of solvents, which may lead to new ways to use SWNTs in diverse applications.

Based on the copolymerization methods, other similar structure triblock copolymers have been synthesized: polylactide-*b*-polyimide-*b*-polylactide, poly(2-methyl-2-(allyloxycarbonyl)propylenecarbonate)-*b*-polyimide-*b*-poly(2-methyl-2-(allyl-oxycarbonyl)-propylene carbonate) and the epoxidized derivative. The tensile strength, modulus, and elongation of the best composite film increases by 40%, 34%

and 26% compared to the neat epoxy resin, which was fabricated in a low boiling point organic solvent (THF). By introducing the alkene groups on the end blocks, we achieve further functionalization, attaching the epoxy groups on the blocks, to achieve chemical reactivity with the epoxy resin. This block copolymer synthesis method can also be applied to other functionality other than epoxy which will pave the way for more applications of polyimides and nanomaterials.

6.2 Recommendations of future work

Due to high modulus, high tensile strength, high toughness, low density and non-corrosive, carbon fiber (CF) reinforce composite attract lots of researchers' attention.¹⁵⁰⁻¹⁵⁴ They are widely used in aerospace, automobile, sports and defence industry. The bare CF surface have a relatively small specific surface area, which decreases the best mechanical performance. To overcome this shortcoming, various surface treatment, such as plasma treatment, chemical functionalization, nanomaterial grafting, are applied to improve interfacial properties.¹⁵⁵⁻¹⁵⁷ The hairy CNTs coating on CF surface show highest specific surface area enhancement at same density variation. Meanwhile, CNTs could pin into and interlock the CF and matrix. The deposition of CNTs onto the CF surface have been proposed by chemical grafting, electrodeposition (ED) and CVD, which all could form hairy CNT coating on CF fiber. However, chemical functionalization cause defect on both CF and CNTs. ED process could only deposit CNTs onto CF which are at outside of the bundles because inside the CF bundle, there is no electric field that could force CNTs in solution to deposit onto the CF surface.

The excellent mechanical property and good corrosion resistance of CNTs make them gain broad application in polymer composite reinforcement. Normally,

MWCNTs or SWNTs are directly dispersed into the Epoxy with assistance of dispersant polymer. The covalent bond between the epoxy molecular and individually dispersed CNT could dramatically increase the Young's modulus, tensile strength and stiffness of the composite.^{158, 159} Recently, the hairy CNTs are grafted onto the CF surface by chemical modification, chemical vapor deposition (CVD) method and electrodeposition process to improve the interaction between CF and epoxy matrix. For example, poly(ether ketone) and 3-aminopropyltriethoxysilane were respectively used as coupling agent to obtain hairy CNTs coated CF.^{160, 161} With hairy CNTs coating, the interfacial interaction between CF and epoxy matrix is greatly enhanced. However, the two grafting process are too complicated and many defects which decrease the strength of CF are introduced onto the fiber surface for chemical grafting. So electrodeposition method is developed to form hairy CNT coating out of the CF.^{162, 163} The CNTs should be strongly acid treated to generate more negative charges on CNTs. However, the defect decrease the internal tensile strength of the CNT and therefore, the mechanical properties of the composite have no remarkable improvement.

Hence, a good dispersant should be applied in order to disperse the CNTs on the carbon fibers. Well-dispersed carbon nanotubes will provide more surface area so that there will be more interaction between carbon fibers and the epoxy matrix. Previously we use polyimide-*graft*-bisphenol A diglyceryl acrylate (PI-BDA) to disperse the hairy carbon nanotubes, but this dispersant is not compatible with epoxy, which did not show improvement in the mechanical properties. And it needs DMF solvent to disperse CNTs. The use of high boiling point solvent brings some difficulties during the composite processing. In order to get composites with better properties, the triblock copolymers may be used in this hairy composite system to get better mechanical properties.

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