<table>
<thead>
<tr>
<th>Title</th>
<th>Synthesis of polycaprolactone-polyimide-polycaprolactone triblock copolymers via a 2-step sequential copolymerization and their application as carbon nanotube dispersants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Liu, Chengyin; Liu, Bo; Chan-Park, Mary B.</td>
</tr>
<tr>
<td>Date</td>
<td>2017</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10220/45024">http://hdl.handle.net/10220/45024</a></td>
</tr>
<tr>
<td>Rights</td>
<td>© 2017 The Royal Society of Chemistry. This is the author created version of a work that has been peer reviewed and accepted for publication by Polymer Chemistry, The Royal Society of Chemistry. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<a href="http://dx.doi.org/10.1039/C6PY01933A">http://dx.doi.org/10.1039/C6PY01933A</a>].</td>
</tr>
</tbody>
</table>
Synthesis of Polycaprolactone-Polyimide-Polycaprolactone Triblock Copolymers via a 2-step Sequential Copolymerization and their Application as Carbon Nanotube Dispersants

Chengyin Liu, Bo Liu and Mary B. Chan-Park

Polyimides have attractive properties such as strong interaction with 1D/2D carbon nanomaterials but their solubilities in common organic solvents are limited. We report a new synthesis route for triblock copolymers of polycaprolactone-polyimide-polycaprolactone (PCL-PI-PCL) via polycondensation followed by ring-opening polymerization. The prepared OH-PI-OH homopolymer precursors were reacted with two equivalents of stannous (II) octoate (Sn(Oct)$_2$) to afford α,ω-dihydroxy-terminated polyimide macroinitiators which can polymerize with ε-caprolactone to obtain the final triblock copolymers (PCL-PI-PCL). Four different molecular weights of PCL-PI-PCL triblock copolymers with different lengths of PCL and PI blocks were synthesized to assess the best composition for carbon nanotube dispersion in a low boiling organic solvent (tetrahydrofuran, THF). The polyimide block interacts strongly with single walled carbon nanotubes (SWNTs) through charge transfer, as shown by Raman spectroscopy, while the polycaprolactone block has a good solubility in THF. An optimised triblock copolymer disperses the carbon nanotubes in THF well even after standing for 1 h, while the PI homopolymer-dispersed SWNTs settled completely under the same conditions. We applied the new PCL-PI-PCL in SWNT-reinforced epoxy composites with the use of THF as the casting solvent. The optimised triblock copolymer-dispersed SWNTs (2 wt%) increased the tensile strength, modulus, and elongation at maximum stress by 74%, 35%, and 62% respectively compared to neat resin blend. The new synthesis route of the triblock copolymer amenable to the synthesis of diverse PI-based triblock copolymers with various desired functionalities for myriad applications, such as for carbon nanotubes-reinforced epoxy-based composites, water-based antibacterial dispersions, etc.

Introduction

Polyimides are high-performance aromatic materials with interesting properties such as high glass transition temperatures and strong interaction with 1D/2D carbon nanomaterials. We had previously shown that polyimides (PI) were very good dispersing agents for carbon nanotubes because of their strong π-π interaction with carbon nanotube side walls. However, they were only soluble in polar aprotic solvents such as DMSO, NMP and DMF. Their poor solubilities and incompatibility with common organic solvents such as THF, chloroform and acetone limited their 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 (PE-PI-PE) has not been reported. Ju et al synthesized a triblock polycaprolactone-block-polyimide-block-polycaprolactone (PCL-PI-PCL), for use as a dielectric material, via “grafting to” of PCL-furyl amine to maleimide-PI. 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 was reversible, so the triblock may decompose with heating. Other polyimide-vinyl block copolymers have been synthesized via atom transfer radical polymerization (ATRP), including polyimide-graft-poly(ethylene oxide) and poly(2-(methyl methacrylate)-block-polyimide-block-poly(2-(methyl methacrylate)). Polyimide-polyester block copolymers have hitherto not been directly synthesized. Ring-opening polymerization has not previously been employed in 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 nanomaterials, field-effect transistors, biosensors, etc. Their intrinsic mechanical, electrical and optical properties are outstanding. However, realization of these properties in practice typically depends on good dispersion of SWNTs in common solvents such as THF, dichloromethane (DCM), acetonitrile, etc. The high surface area of nanotubes results in strong intertube Van der Waals forces so that they easily aggregate into bundles. Nanotube dispersing agents ought to have strong affinity for the nanotubes as well as good solubilities in common solvents, which may entail contrasting...
Table 1 Synthesis of OH-bifunctional polyimides.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ratio in feed (BPADA)/(HAB)/(APA)</th>
<th>Mₙ(Da)</th>
<th>PDI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP1</td>
<td>100/75/50</td>
<td>6000</td>
<td>1.78</td>
</tr>
<tr>
<td>HP2</td>
<td>100/90/20</td>
<td>14700</td>
<td>1.65</td>
</tr>
<tr>
<td>HP3</td>
<td>100/95/10</td>
<td>35800</td>
<td>1.80</td>
</tr>
</tbody>
</table>

The four triblock copolymers (TB1a, TB1b, TB2 and TB3, see Table 2) were characterized with NMR, GPC and FTIR. SWNTs dispersions, using PCL-PI- PCL triblock copolymers (TBs) and the homopolymer (HP1), were characterized with UV-VIS-NIR, AFM, TEM, and Raman spectroscopy. We found that TB1a triblock copolymer most effectively dispersed SWNTs. The central PI block noncovalently adsorbed on carbon nanotubes while the two ends of PCL blocks provided good solubilities in THF solvent (a model low boiling point solvent). There appeared to be an optimum ratio of PI to PCL block length for the triblock (as with TB1a) to achieve excellent SWNT dispersion in THF solvent. Further, epoxy composites reinforced with SWNTs dispersed by TB1a in THF were fabricated and the tensile properties were improved by incorporation of the SWNTs.

Results and discussion

Design and Synthesis of OH-PI-OH Homopolymers and PCL-PI-PCL Copolymers

The synthesis route of OH-PI-OH homopolymers and PCL-PI-PCL triblock copolymers was shown in Scheme 1. The OH-PI-OH homopolymers were 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 yellowish polyimide was formed after thermal imidization. Two terminal OH groups of polyimide were observed in Fig. S1(b) (δ(OH) = 4.76 ppm, δ(CH2-OH) = 3.50 ppm and δ(CH2-CH2) = 2.77 ppm). The measured molecular weights (Mₙ) of various OH-PI-OH increased from 6,000 Da to 14,700 Da and to 35,800 Da with increasing ratio of HAB monomers; three polyimide homopolymers, labelled as HP1 to HP3 (Table 1), were synthesized.

The as-prepared OH-PI-OH (HP1 to HP3) can easily react with Sn(Oct), to yield an α,ω-O-Sn(Oct) terminated PI initiator, which can undergo ring-opening polymerization with cyclic ester monomers, such as ε-caprolactone, lactones and carbonates etc. We made four PCL-PI-PCL triblock copolymers, labelled TB1a, TB1b, TB2 and TB3, from the HP1 to HP3 center blocks (Table 2). The four triblock copolymers were characterized by NMR and GPC. For example, successful synthesis of the triblock copolymer TB1a was confirmed with ¹H NMR and FTIR. The chemical shifts at 4.00, 2.30, 1.56 and 1.32 ppm, which were absent in homopolymer spectra, were assigned to the PCL block (Fig. S1). The FTIR spectrum of the triblock copolymer had bands around 2800–3000 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 HP1 and TB1a (Fig. S2). The syntheses of the other PI homopolymers (HP2, HP3) and PCL-PI-PCL triblock copolymers (TB1b, TB2, and TB3) were also confirmed by ¹H NMR (Fig. S3 to Fig. S7).
Table 2 PCL-PI-PCL triblock copolymers initiated by different polyimide homopolymers in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Design [I]:[M]</th>
<th>Initiator (M_w (Da))</th>
<th>TB measured M_n (Da)</th>
<th>Actual Repeating PI units (m)</th>
<th>Actual Repeating CL Units (n)</th>
<th>Actual Ratios of n:m:n</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB1a</td>
<td>1:100</td>
<td>HP1 (6000)</td>
<td>13200/1.40</td>
<td>9</td>
<td>60</td>
<td>3:1:3</td>
</tr>
<tr>
<td>TB1b</td>
<td>1:200</td>
<td>HP1 (6000)</td>
<td>19700/1.25</td>
<td>9</td>
<td>120</td>
<td>6:1:6</td>
</tr>
<tr>
<td>TB2</td>
<td>1:200</td>
<td>HP2 (14700)</td>
<td>17700/1.43</td>
<td>21</td>
<td>24</td>
<td>1:2:1</td>
</tr>
<tr>
<td>TB3</td>
<td>1:200</td>
<td>HP3 (35800)</td>
<td>39300/1.65</td>
<td>51</td>
<td>28</td>
<td>3:10:3</td>
</tr>
</tbody>
</table>

a Molar ratio of polyimide macroinitiator and caprolactone 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.

Fig. S11 showed the GPC curves of OH-PI-OH homopolymers (HP1, HP2, and HP3) and also the PCL-PI-PCL triblock copolymers (TB1a, TB1b, TB2, TB3). The molecular weights (M_w) of PI and PCL-PI-PCL were summarized in Table 1 and Table 2, respectively. The molecular weights of all the triblock copolymers exceeded those of the corresponding OH-PI-OH polymers. For example, M_w of the homopolymer HP1 was 6000 Da, but that of TB1a (the triblock made from HP1) was 13200 Da. The PDI of the triblock remained narrow (1.2 to 1.8, Table 2), indicating that the PCL-PI-PCL was a true triblock copolymer and not a mixture.

The solubilities of these polymers in common solvents were shown in Table S1 and Table S2. TB1a and TB1b were soluble in more solvents because they had the short polyimide center blocks; TB3 was soluble in only a few solvents because of the high molecular weight of its polyimide block.

**SWNTs Dispersion and Interfacial Bonding with PCL-PI-PCL**

SWNT dispersions in THF using various PCL-PI-PCL triblock copolymers as the dispersing agents were quantitatively evaluated using UV-VIS-NIR absorption spectra and the Beer-Lambert law (see Experimental Details). The absorbance of dilute polymer TB1a solutions (0.025, 0.05, 0.075, 0.125 and 0.2 mg/mL) with SWNTs (mass ratio of TB1a and SWNTs = 2:1) in THF was measured and the absorbance at 700 nm was plotted against SWNT concentrations (Fig. 1). A linear-least-squares fit to the data gave a slope of 11.7, which was the extinction coefficient (i.e., ε = 11.7 mL mg⁻¹ cm⁻¹) for back-calculating the SWNTs concentration in other solutions (The dispersing agent and solvent absorbance is low and smoothly varying at the wavelength of our measurements, and so can be easily subtracted from absorbance measurements of dispersed SWNTs) (Fig. S13).

We evaluated the different TBs (TB1a, TB1b, TB2 and TB3) for dispersing SWNTs in THF (Fig. 2). The nanotube concentrations of the supernatants of various TB/SWNT dispersions subjected to various settling regimes, i.e. specifically immediately after sonication, or sonication followed by centrifugation at 6000 rpm or 10000 rpm each for 10 mins, were evaluated by UV-VIS-NIR and the Beer-Lambert law. For all the TBs, some SWNTs settled to the bottom after centrifugation at 6000 rpm or 10000 rpm, while some still remained in the solvent (Fig. 2). After centrifugation at the higher speed (10000 rpm), TB1a dispersed SWNTs solution had the highest nanotube concentration (Fig. 2(a)), indicating that TB1a was the most effective in dispersing SWNTs. TB2 — dispersed SWNTs solution was almost clear and the color of TB1b-dispersed SWNTs solution was light after centrifugation.
Fig. 2 (a) SWNT concentrations of different molecular weight PCL-PI-PCL dispersed in THF under different conditions: immediately after sonication, after centrifugation at 6000 rpm for 10 mins, and after centrifugation at 10000 rpm for 10 mins; (b) Photographs of PCL-PI-PCL dispersed SWNTs in THF after centrifugation at 10000 rpm.

(Fig. 2(b)), indicating that most SWNTs have settled to the bottom. Comparing the four TB dispersants, the length of PCL should be moderate; too long (TB1b) or too short PCL block (TB2) impaired the dispersion; longer PI block while keeping the PCL block length constant was helpful for the nanotube dispersion, which was why TB3 was better than TB2 in dispersing the nanotubes. In order to confirm this statement, more TBs with different lengths of PCL blocks were made (TB1c, TB1d and TB1e, see Table S3). They were all initiated by same polyimide (HP1) and their molecular weights are summarized together with TB1a and TB1b in Table S3. The synthesis of TB1c, TB1d and TB1e was confirmed by 1H NMR spectra (Fig. S8-10) and GPC curves (Fig. S12). The molecular weights of newly synthesized TB1c and TB1d are 9400 and 11500 Daltons, whereas TB1e molecular weight is 16600 Dalton, intermediate between TB1a and TB1b. The concentration of SWNTs in THF dispersed by different TBs are calculated by UV-Vis-NIR curves and are shown in Fig. S14. Immediately after sonication, the concentration of SWNTs are all around 0.2 mg/mL, while after centrifugation at 6000 rpm and 10000 rpm, the concentration of SWNT using TB1a and TB1e dropped the least compared to the other 3 ratios, indicating that a better dispersant is achieved by optimizing the ratio of PI to PCL block chain length to be around 1:3. Considering these various factors (different PCL block length ratio and PI length), TB1a was among the best TBs to effectively disperse SWNTs in THF. So we choose TB1a as a dispersant to further evaluate the dispersion of SWNTs and make some composites.

We also compared the efficacy of the polyimide homopolymer (HP1) center block versus TB1a triblock copolymer in suspending SWNTs in THF after centrifugation, by comparing the SWNT content in solutions of HP1/SWNT versus that of TB1a/SWNT (Fig. 3(a)). Immediately after sonication, both TB1a/SWNT and HP1/SWNT dispersion had nearly the same nanotube concentration ~50 mg/L. After centrifugation, the nanotube concentrations in the supernatants of TB1a/SWNT decreased to 33 and 28 mg/L for 6000 rpm and 10000 rpm respectively, which were much higher than the corresponding values of HP1/SWNT (6 and 3 mg/L) after similar centrifugation regimes (Fig. 3(a)), indicating that the dispersion of SWNTs in THF was greatly improved by incorporation of PCL end blocks in the copolymers. We also compared the settling of SWNTs upon standing after 1 h using HP1 (control) versus TB1a as dispersing agents; Fig. 3(b) and 3(c) showed photographs of SWNTs dispersed in THF after standing for 1 h and immediately after sonication respectively. After sonication, both of the solutions were black (Fig. 3(b)). But after standing for 1 h, the SWNTs dispersed in HP1 solution mostly settled, while no obvious aggregates were observed in the TB1a/SWNT solution, indicating homogeneous dispersion that was stable on standing was achieved with the TB1a triblock polymer (Fig. 3(c)). Because the solubility of PCL in THF was very good (Table S2), it can improve the solubility of SWNTs in the solvent and help to form a more stable SWNT solution.

To further examine the nanotube dispersion and morphology, TEM and AFM images of the dispersed SWNTs were obtained. The HP1-dispersed SWNTs, which were used as the control, formed bundles with large diameters of about 30 nm (Fig. 4(a)), while the majority of the TB1a-dispersed SWNTs were observed in smaller bundles with diameters of around 5 nm (Fig. 4(b)). At a lower magnification (x8000) (Fig. 4(bii)), it can be seen that the carbon nanotubes were wrapped with the PCL-PI-PCL polymer (TB1a) and also intercalated by the
protonated with a pH of 7.4. The disc electrophoresis was performed at 100 V for 20 min.

The result obtained from the disc electrophoresis revealed that the charge on the nanoparticles was negative, as shown in Figure 1(b), indicating the successful surface modification of the CQDs with carboxylic groups.


disc electrophoresis was performed at 100 V for 20 min.

The result obtained from the disc electrophoresis revealed that the charge on the nanoparticles was negative, as shown in Figure 1(b), indicating the successful surface modification of the CQDs with carboxylic groups.

This journal is © The Royal Society of Chemistry 20xx
J. Name., 2013, 00, 1-3 | 5

Please do not adjust margins

Please do not adjust margins

Please do not adjust margins
Fig. 9 FE-SEM images of fracture surface of TB1a/epoxy/SWNT with 2 wt% SWNT loading at (a) low magnification (×5000) and (b) high magnification (×20000).

SWNTs Dispersion in TB1a/epoxy Films and the Mechanical Properties of the Composite Films

As TB1a was the best SWNT dispersant of the four TBs synthesized, we used it as the dispersant of nanotubes for epoxy composite fabrication with a range of SWNT loadings. Some typical TB1a/epoxy/SWNT composite films of different loadings were shown in Fig. 7. The films appearance are quite dark and homogeneous for all three loadings (2 wt%, 4 wt% and 6 wt%). The mechanical properties of the films are summarized in Table 3. Typical stress-strain curves of the composite films were shown in Fig. 8. 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 TB1a/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.

Fracture surfaces of the composite films after tensile testing were shown in Fig. 9. There were some pull-outs 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 (TB1a) was an effective SWNT dispersant for epoxy composites.

Experimental

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. Polycaprolactone (average Mn~14,000 Da and average Mw~10000 Da) as control was purchased from Sigma-Aldrich. 3,3′-Dihydroxy-4,4’-diaminobiphenyl (HAB, 97%) was purchased from Tokyo Chemical Industry and purified by recrystallization from N,N’-dimethylformamide (DMF)/water mixture. 4-Aminophenethanol (APA) was purified by recrystallization from ethanol. 2,2-Bis[4-[(3,4-dicarboxyphenoxy)phenyl]]propane anhydride (BPADA) was dissolved in acetic anhydride and toluene and refluxed; the solution was then cooled overnight and the solvent removed under reduced pressure at 70 °C. Epoxy resin (Part A: EPR L20 and Part B: EPH 960) was obtained from Bakelite. 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 purification.

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 over 30 mins. 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 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. Other molecular weights of OH-Pi-OH were synthesized by the same procedure as above with various ratios of the three monomers (Table 1).

One-pot synthesis of triblock copolymer PCL-Pi-PCL

In a glove box, OH-Pi-OH (0.8 g, 0.1 mmol) (Mn = 12100 Da) 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 stirred for 6 h. Fresh 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 dissolved in NMP and precipitated in methanol 2 times followed by drying overnight at 70 °C for 24 h under reduced pressure. Other PCL-Pi-PCL triblock copolymers with different molecular weights (Table 2) synthesized via similar procedure.

Dispersion of SWNTs with various dispersing agents in THF

The concentration of SWNTs in solution can be estimated from the Beer-Lambert law, A = eclc, where A is the absorbance due to SWNTs at a particular wavelength (here we chose 700 nm), ε is the extinction coefficient, l is the path length (1 cm for our cell), and c is the concentration. To determine the extinction coefficient (ε), the absorbance of dilute SWNTs solutions (0.025, 0.05, 0.075, 0.125 and 0.2 mg/mL in THF with dispersing agent TB1a, prepared by tip
sonication for 30 mins (1 and 1 second on/off)) was measured and the absorbance at 700 nm was plotted against SWNT concentrations. The extinction coefficient was the slope of the absorbance/SWNT concentration relation.

0.2 mg/mL solutions of TBs/SWNT (mass ratio of polymer and SWNTs = 2:1) in THF was prepared by tip sonication (150 W, 60%) for 30 mins (1 and 1 second on/off) and the absorption at 700 nm was measured immediately and after centrifugation at 6000 rpm for 10 mins and 10000 rpm for 10 mins. A 0.05 mg/mL solution of TB1a/SWNT (mass ratio of polymer and SWNTs = 2:1) in THF was prepared by tip sonication (150 W, 60%) for 30 mins (1 and 1 second on/off) and the absorption at 700 nm was measured immediately and after centrifugation at 6000 rpm for 10 mins and 10000 rpm for 10 mins. Comparison measurements were made of HP1/SWNT in THF at the same concentration and centrifuge preparation.

Fabrication of TB1a/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 TB1a/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 mount of pre-cured epoxy. After thorough mixing by bath sonication, the solution was cast on glass. After evaporating the solvent, the films were fully dried in vacuum oven at 40 °C. The films were then peeled from the glass and cured at 130 °C for 3 h.

Structure analysis and characterization

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) performed with a Shimadzu LC-20A Series GPC system equipped with a pump, a BC-PL gel mixed column, and a RID. FTIR measurements. We also thank the funding support from a Singapore Ministry of Health Industry Alignment Fund (MOE2013-3-002), a Singapore Ministry of Education Tier 3 grant (MOE2013-T3-1-002), a Singapore Ministry of Health Industry Alignment Fund (NMRC/MOHIAFCAT2/003/2014), and the NTU iFood grant.

Acknowledgements

Liu Chengyin thanks Nanyang Technological University for the support of her Ph.D. We thank Dr. Wang Yilei for his help in AFM measurements and Zhang Penghui for his help in TEM measurements. We also thank the funding support from a Singapore Ministry of Education Tier 3 grant (MOE2013-T3-1-002), a Singapore Ministry of Health Industry Alignment Fund (NMRC/MOHIAFCAT2/003/2014), and the NTU iFood grant.

References

Electronic Supplementary Information

Synthesis of Polycaprolactone-Polyimide-Polycaprolactone Triblock Copolymers via a 2-step Sequential Copolymerization and their Application as Carbon Nanotube Dispersants

Chengyin Liu a†, Bo Liu b†, Mary B. Chan-Park a,b* 

a School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459, Singapore
b Lee Kong Chien School of Medicine, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459, Singapore

Fig S1 1H NMR of (a) PCL (300M, CDCl3, 25 °C), (b) HP1 (300M, d6-DSMO, 25 ºC) and (c) TB1a (300M, d6-DSMO, 25 ºC) (*: NMP residue).
Fig S2 FTIR spectra of PCL, HP1 and TB1a.
Fig S3 1H NMR spectrum of HP2 (300M, d6-DSMO, 25 °C).
Fig S4 1H NMR spectrum of HP3 (300M, d6-DSMO, 25 °C).
Fig S5 1H NMR spectrum of TB1b (300M, d6-DSMO, 25 °C).
Fig S6 1H NMR spectrum of TB2 (300M, d6-DSMO, 25 °C).
Fig S7 1H NMR spectrum of TB3 (300M, d6-DSMO, 25 °C).
Fig S8 1H NMR spectrum of TB1c (300M, d6-DSMO, 25 °C).
Fig S9 1H NMR spectrum of TB1d (300M, d6-DSMO, 25 °C).
Fig S10 1H NMR spectrum of TB1e (300M, d6-DSMO, 25 °C).
Fig S11. GPC curves of OH-PI-OH (HP1, HP2, HP3) and PCL-PI-PCL (TB1a, TB1b, TB2, TB3).
Fig S12. GPC curves of three new PCL-PI-PCL synthesized from HP1 (TB1c, TB1d, TB1e).
Fig S13 UV-Vis-NIR absorption spectrum of TB1a polymer in THF.
Fig S14 SWNT concentrations of different molecular weight TBs ((a) TB1a, TB1b, TB1c, TB1d, TB1e (b) TB1c, TB2, TB3) dispersed in THF under different conditions: immediately after sonication, after centrifugation at 6000 rpm for 10 mins, and after centrifugation at 10000 rpm for 10 mins.
Table S1 Solubility of different PCL-PI-PCL triblock polymers.
Table S2 Solubility of PCL, OH-PI-OH (HP1) and PCL-PI-PCL (TB1a).
Table S3 PCL-PI-PCL triblock copolymers initiated by HP1.
Supporting Figures and Tables

Fig. S1 $^1$H NMR of (a) PCL (300M, CDCl$_3$, 25 °C), (b) HP1 (300M, d$_6$-DSMO, 25 °C) and (c) TB1a (300M, d$_6$-DSMO, 25 °C) (* : NMP residue).
Fig. S2 FTIR spectra of PCL, HP1 and TB1a.
Fig. S3 $^1$H NMR spectrum of HP2 (300M, $d_6$-DSMO, 25 °C).
Fig. S4 $^1$H NMR spectrum of HP3 (300M, d$_6$-DSMO, 25 °C).
Fig. 55 $^1$H NMR spectrum of TB1b (300M, $d_6$-DMSO, 25 °C).
Fig. S6 $^1$H NMR spectrum of TB2 (300M, $d_6$-DSMO, 25 °C).
Fig. 57 $^1$H NMR spectrum of TB3 (300M, $d_6$-DSMO, 25 °C).
Fig. S8 $^1$H NMR spectrum of TB1c (300M, $d_6$-DSMO, 25 °C).
Fig. 59 $^1$H NMR spectrum of TB1d (300M, $d_6$-DSMO, 25 °C).
Fig. S10 $^1$H NMR spectrum of TB1e (300M, d$_6$-DSMO, 25 °C).
**Fig. S11** GPC curves of OH-PI-OH (HP1, HP2, HP3) and PCL-PI-PCL (TB1a, TB1b, TB2, TB3).

**Fig. S12** GPC curves of three new PCL-PI-PCL synthesized from HP1 (TB1c, TB1d, TB1e).
Fig. S13 UV-Vis-NIR absorption spectrum of TB1a polymer in THF.
Fig. S14 SWNT concentrations of different molecular weight TBs ((a) TB1a, TB1b, TB1c, TB1d, TB1e (b) TB1c, TB2, TB3) dispersed in THF under different conditions: immediately after sonication, after centrifugation at 6000 rpm for 10 mins, and after centrifugation at 10000 rpm for 10 mins.
**Table S1** Solubility of different PCL-PI-PCL triblock polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>NMP</th>
<th>DMF</th>
<th>THF</th>
<th>CHCl3</th>
<th>DCM</th>
<th>Acetone</th>
<th>Hexane</th>
<th>MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB1a</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>TB1b</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>TB2</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>TB3</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

+, good solubility; -, insoluble after 30 mins

**Table S2** Solubility of PCL, OH-PI-OH (HP1) and PCL-PI-PCL (TB1a).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>NMP</th>
<th>DMF</th>
<th>THF</th>
<th>CHCl3</th>
<th>DCM</th>
<th>Toluene</th>
<th>Hexane</th>
<th>MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>TB1a</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HP1</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

+, good solubility; -, insoluble after 30 mins

**Table S3** PCL-PI-PCL triblock copolymers initiated by HP1 (Mn = 6000 Da).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Design [I]:[M]a</th>
<th>TB measured Mn (Da)/PDb</th>
<th>Actual Repeating PI units (m)c</th>
<th>Actual Repeating CL Units (n)c</th>
<th>Actual Ratios of n:m:n</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB1c</td>
<td>1:25</td>
<td>9400/1.46</td>
<td>9</td>
<td>20</td>
<td>1:1:1</td>
</tr>
<tr>
<td>TB1d</td>
<td>1:50</td>
<td>11500/1.61</td>
<td>9</td>
<td>46</td>
<td>5:2:5</td>
</tr>
<tr>
<td>TB1a</td>
<td>1:100</td>
<td>13200/1.40</td>
<td>9</td>
<td>60</td>
<td>3:1:3</td>
</tr>
<tr>
<td>TB1e</td>
<td>1:150</td>
<td>16600/1.55</td>
<td>9</td>
<td>90</td>
<td>5:1:5</td>
</tr>
<tr>
<td>TB1b</td>
<td>1:200</td>
<td>19700/1.25</td>
<td>9</td>
<td>120</td>
<td>6:1:6</td>
</tr>
</tbody>
</table>

a Molar ratio of polyimide macroinitiator and caprolactone 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.