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

Supporting Figures and Tables

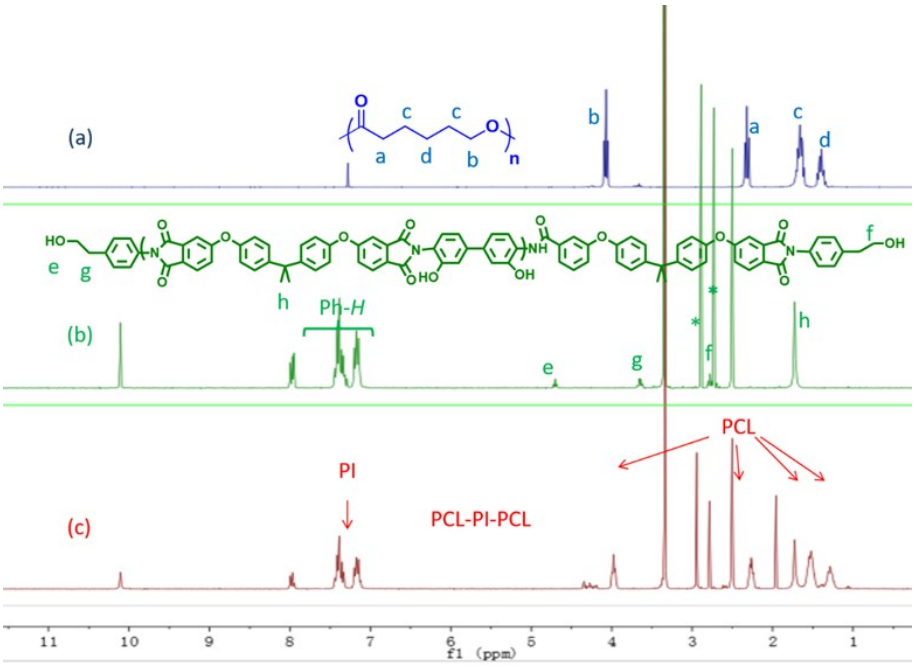

Fig. S1 ^{1}H NMR of (a) PCL (300M, $CDCl_3$, 25 °C), (b) HP1 (300M, d_6-DSMO, 25 °C) and (c) TB1a (300M, d_6-DSMO, 25 °C) (* : NMP residue).

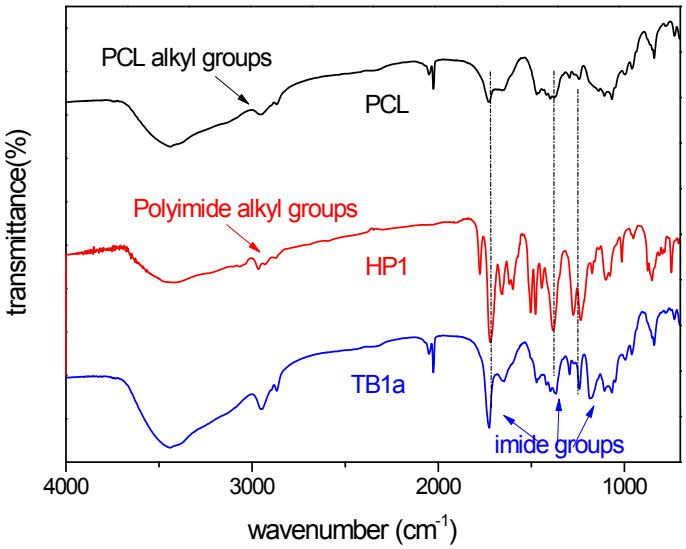

Fig. S2 FTIR spectra of PCL, HP1 and TB1a.

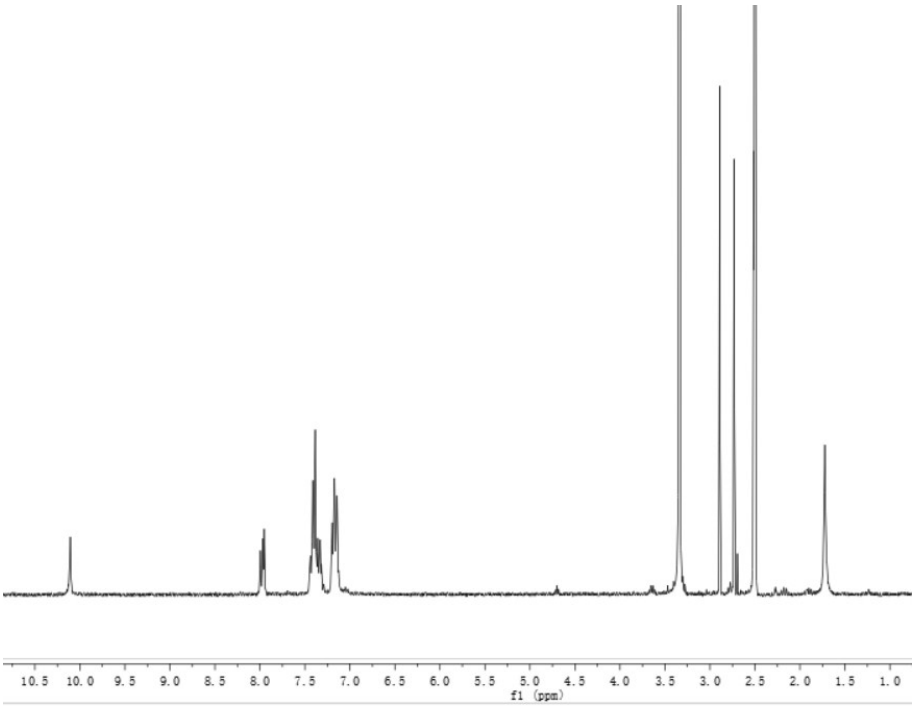

Fig. S3 ^{1}H NMR spectrum of HP2 (300M, d_6-DSMO, 25 ^{o}C).

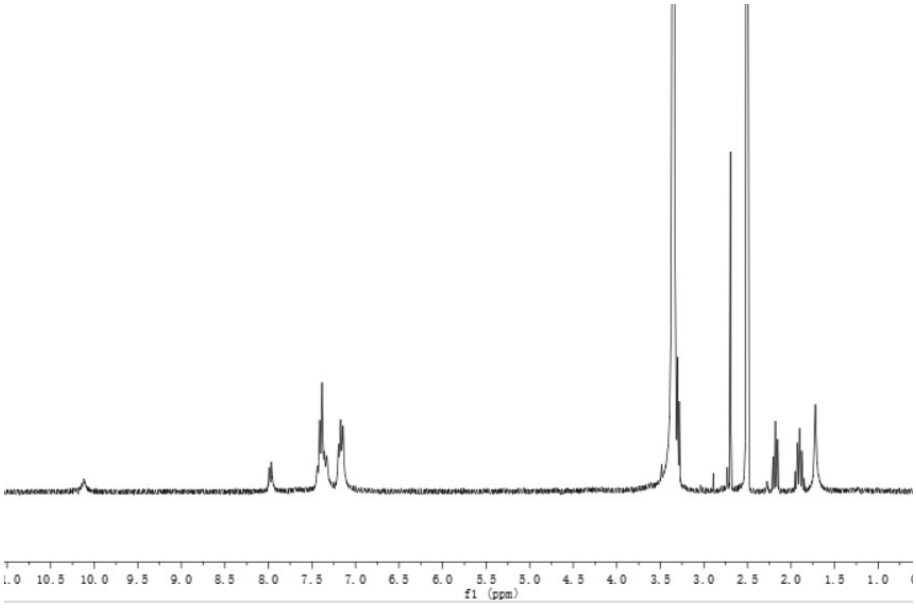

Fig. S4 ^{1}H NMR spectrum of HP3 (300M, d_6-DSMO, 25 ^{o}C).

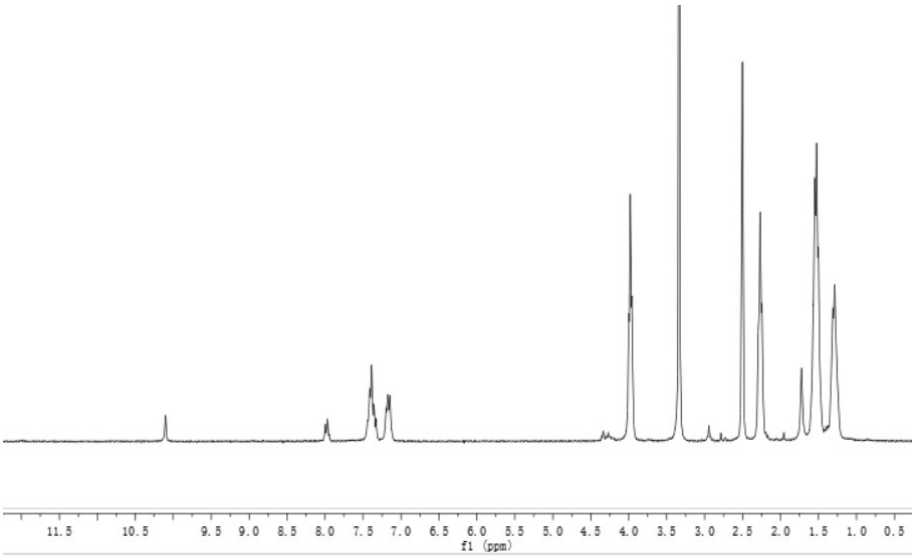

Fig. S5 ^{1}H NMR spectrum of TB1b (300M, d_6-DSMO, 25 ^{o}C).

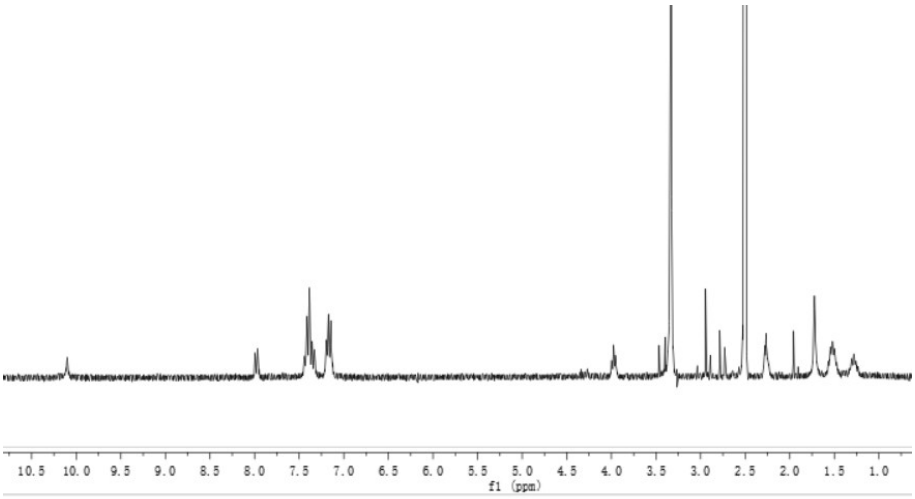

Fig. S6 ^{1}H NMR spectrum of TB2 (300M, d_6-DSMO, 25 ^{o}C).

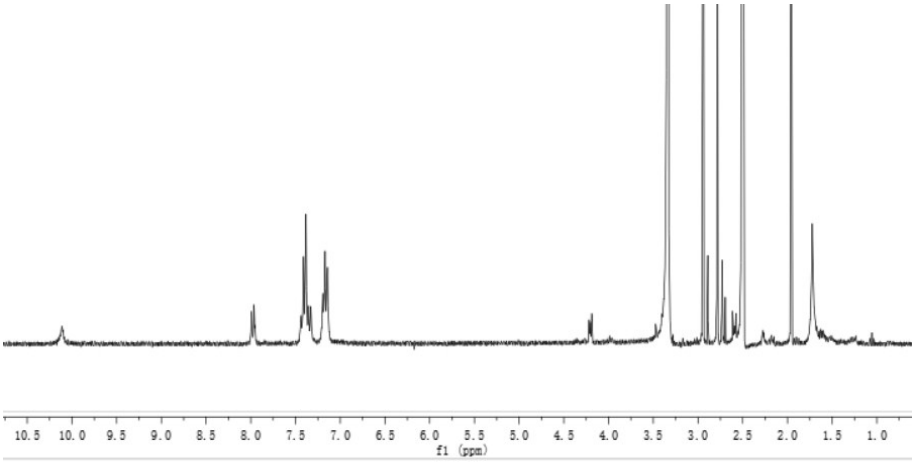

Fig. S7 ^{1}H NMR spectrum of TB3 (300M, d_6-DSMO, 25 ^{o}C).

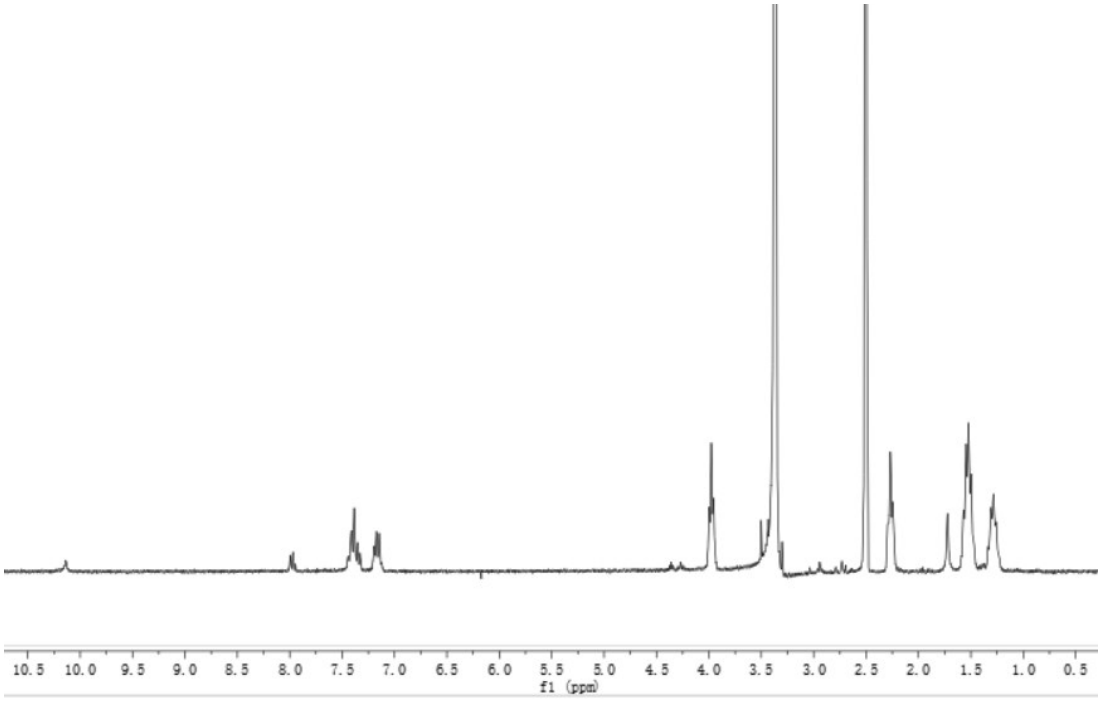

Fig. S8 ^{1}H NMR spectrum of TB1c (300M, d_6-DSMO, 25 ^{o}C).

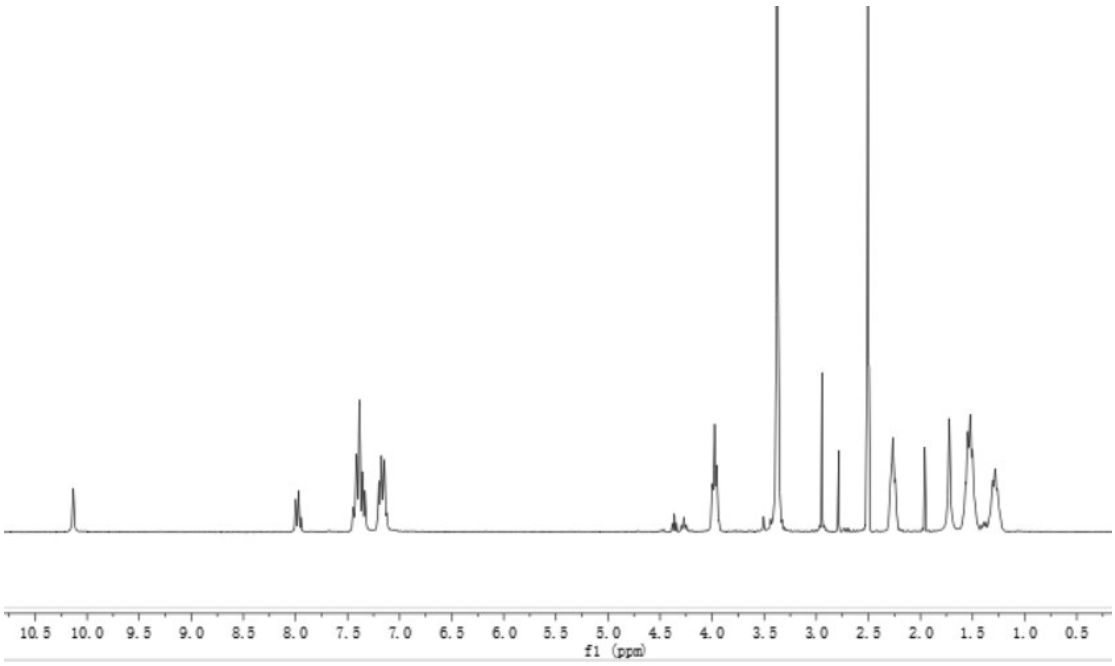

Fig. S9 ^{1}H NMR spectrum of TB1d (300M, d_6-DSMO, 25 ^{o}C).

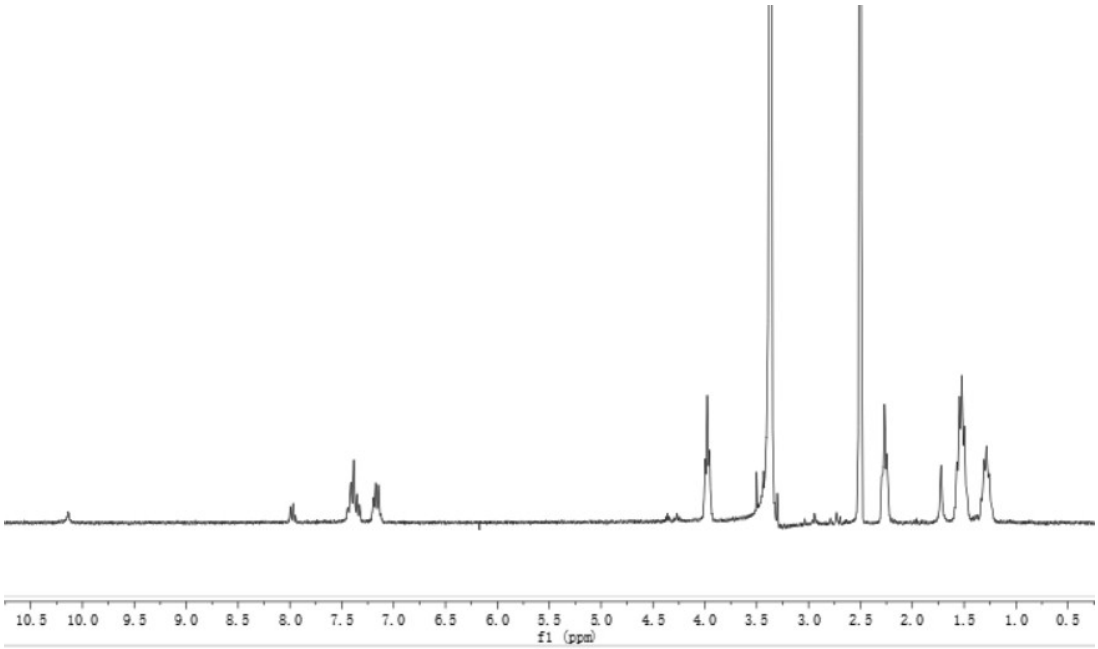

Fig. S10 ^{1}H NMR spectrum of TB1e (300M, d_6-DSMO, 25 ^{o}C).

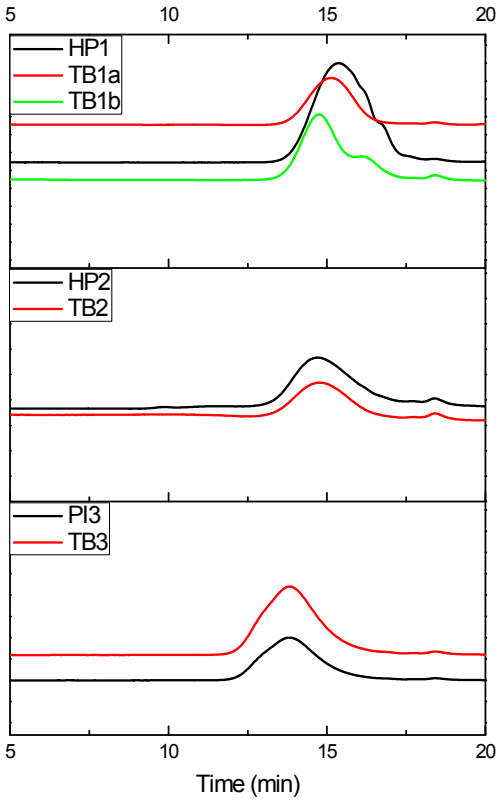

Fig. S11 GPC curves of OH-PI-OH (HP1, HP2, HP3) and PCL-PI-PCL (TB1a, TB1b, TB2, TB3).

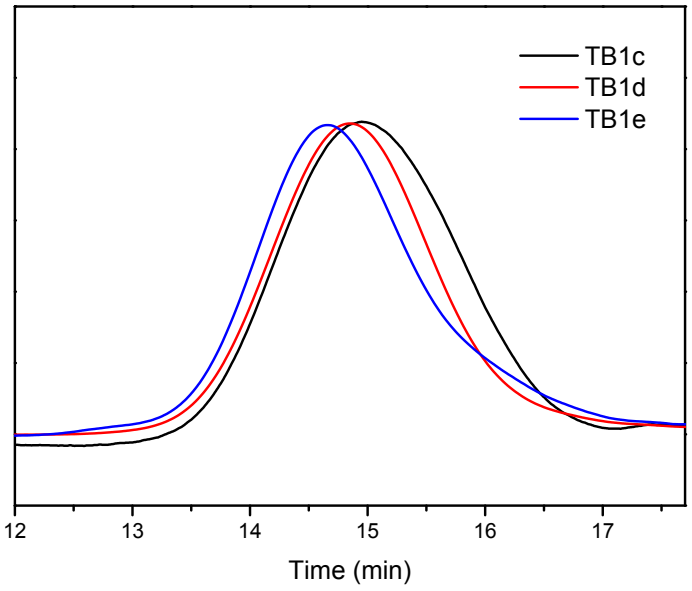

Fig. S12. GPC curves of three new PCL-PI-PCL synthesized from HP1 (TB1c, TB1d, TB1e).

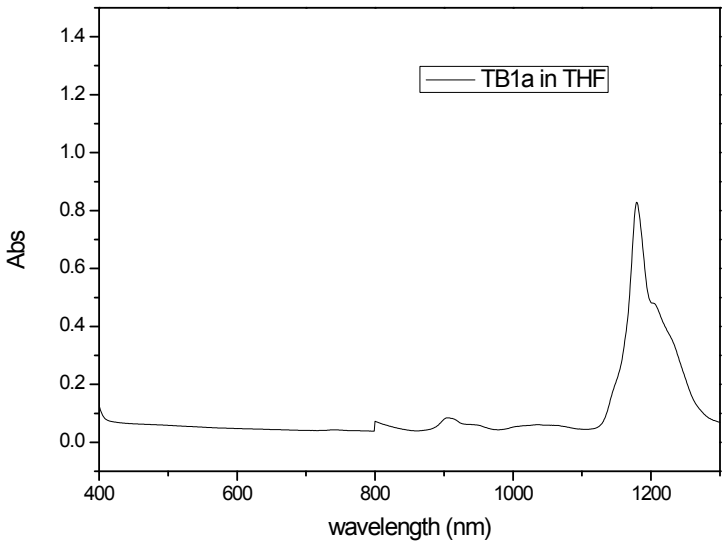

Fig. S13 UV-Vis-NIR absorption spectrum of TB1a polymer in THF.

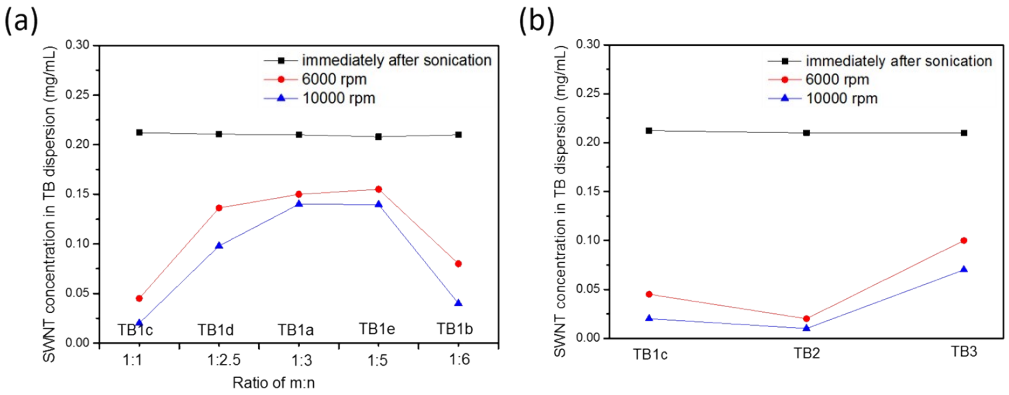

Fig. S14 (see Scheme 1 for meaning of m and n) SWNT concentrations of different molecular weight TBs ((a) TB1a, TB1b, TB1c, TB1d, TB1e (b) TB1c, TB2, TB3) dispersed in THF under different conditions: immediately after sonication, after centrifugation at 6000 rpm for 10 mins, and after centrifugation at 10000 rpm for 10 mins.

Table S1 Solubility of different PCL-PI-PCL triblock polymers.

	solubility							
Polymer	NMP	DMF	THF	CHCl3	DCM	Acetone	Hexane	MeOH
TB1a	+	+	+	+	+	+	+	-
TB1b	+	+	+	+	+	+	-	-
TB2	+	+	+	+	-	-	-	-
TB3	+	+	+	-	-	-	-	-
+, good solubility; -, insoluble after 30 mins								

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

	solubility							
Polymer	NMP	DMF	THF	CHCl3	DCM	Toluene	Hexane	MeOH
PCL	+	+	+	+	+	+	+	-
TB1a	+	+	+	+	+	-	-	-
HP1	+	+	+	-	-	-	-	-
+, good solubility; -, insoluble after 30 mins								

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

Sample	Design [PI]:[CL][a]	TB measured M_n (Da) /PDI[b]	Actual Repeating PI units (m)[c]	Actual Repeating CL Units (2n)[c]	Actual Ratios of n:m:n
TB1c	1:25	9400/1.46	9	20	1:1:1
TB1d	1:50	11500/1.61	9	46	2.5:1:2.5
TB1a	1:100	13200/1.40	9	60	3:1:3
TB1e	1:150	16600/1.55	9	90	5:1:5
TB1b	1:200	19700/1.25	9	120	6:1:6

[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.