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Application of functional diols derived from pentaerythritol as chain extenders in the synthesis of novel thermoplastic polyester-urethane elastomers

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Experimental

Materials and Methods

Benzaldehyde, 5-norbornene-2-carboxaldehyde (endo/exo), 1-thioglycerol, 7-mercapto-4-methylcoumarin and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, subsequently dried over CaH_2) were purchased from Sigma Aldrich. Pentaerythritol 98% and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were purchased from Acros Chemicals. Deuterated dimethyl sulfoxide ($(CD_3)_2SO_4$) were purchased from Apollo Scientific Ltd. Poly(caprolactone) M_w = 2,000 g·mol^{-1} (PCL_{2k}) was received from Perstorp UK Ltd. dicyclohexylmethane 4,4'-diisocyanate ($H_{12}MDI$) was purchased from Tokyo Chemical Industry (TCI) UK Ltd. Dimethyl sulfoxide (DMSO), hydrochloric acid (HCl 37%), and toluene were purchased from Fisher Scientific. All chemicals were used as received from the suppliers unless otherwise stated. ^1H and ^{13}C NMR spectra were obtained on a Bruker DPX-400 spectrometer (400 MHz) at 293 K. All chemical shifts were reported as δ in parts per million (ppm) and referenced to the residual solvent signal ($(CD_3)SO$: ^1H, δ = 2.50 ppm; ^{13}C, δ = 39.52 ppm). Gel permeation chromatography (GPC) was used to determine the molecular weight dispersities ($Đ_M$) and weight average molecular weights (M_w) of synthesised polymers. GPC was conducted in dimethylformamide (DMF), with 0.1% (w/v) LiBr salt using an Varian PL-GPC 50 system equipped with 2 × PLgel 5 µM MIXED-D columns in series and a differential refractive index (RI) detector at a flow rate of 1.0 mL·min^{-1}. The systems were calibrated against Varian Polymer Laboratories Easi-Vial linear poly(methyl methacrylate) (PMMA) standards and analysed by the software package Cirrus v3.3.

2-phenyl-5,5-bis(hydroxymethyl)-1,3-dioxane (C_{Ph}) synthesis:

The benzylidene acetal-functionalised pentaerythritol-based diol was synthesised *via* the acid-catalysed acetal formation from benzaldehyde, modified from previous reports.[1] In a clean round bottom flask, pentaerythritol (50 g, 367 mmol) was suspended in 400 mL of deionised water and heated to 80 °C with stirring until all the solid had dissolved. The pentaerythritol solution was allowed to cool to ambient temperature before the addition of conc. HCl (1.5 mL, 14.8 mmol, HCl 36 wt% in H_2O) with continual stirring for 15 min. Benzaldehyde (42.87 g, 404 mmol) was added drop-wise to the acidified solution over 20 min and allowed to stir for a further 2 hours. The mono-functionalised product formed a white crystalline precipitate which was collected *via* vacuum filtration before being purified by re-crystallisation from hot toluene/THF (90:10) to yield white crystals. Analysis was consistent with previous reports.[2] (36.5 g, yield: 44%) ^1H NMR (400 MHz, DMSO-d_6) δ 7.50 – 7.29 (m, 5H), 5.41 (s, 1H), 4.67 (t, $^3J_{H\text{-}H}$ = 5.3 Hz, 1H), 4.58 (t, $^3J_{H\text{-}H}$ = 5.1 Hz, 1H), 3.93 (d, $^2J_{H\text{-}H}$ = 11.2 Hz, 2H), 3.80 (d, $^2J_{H\text{-}H}$ = 11.2 Hz, 2H), 3.69 (d, $^3J_{H\text{-}H}$ = 5.2 Hz, 2H), 3.26 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.76 (s, C), 128.59 (s, CH), 127.95 (s, 2(CH)), 126.14 (s, 2(CH)), 100.66 (s, CH), 69.06 (s, 2(CH_2)), 60.97 (s, CH_2), 59.48 (s, CH_2).

2-norbornene-5,5-bis(hydroxymethyl)-1,3-dioxane (C_{Nb}) Synthesis[3]:

In a clean round bottom flask, pentaerythritol (13.5 g, 99.2 mmol) was suspended in 100 mL of deionised water and heated to 80 °C with stirring until all the solid had dissolved. The pentaerythritol solution was allowed to cool to ambient temperature before the addition of conc. HCl (330 µL, 3.26 mmol) with continual stirring for a 15 min. 5-Norbornene-2-carboxaldehyde (10 g, 89.2 mmol) was added drop-wise to the acidified solution over 20 min and allowed to stir for a further 2 hours. The mono-functionalised product formed an orange precipitate which was collected *via* vacuum filtration before further purification by silica plug, ethyl acetate as the eluent, and re-crystallisation from hot toluene to yield white crystals (10.8 g, yield: 51 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.15 (dd, $^3J_{H\text{-}H}$ = 5.7, 3.0 Hz, 1H), 5.90 (dd, $^3J_{H\text{-}H}$ = 5.7, 3.0 Hz, 1H), 4.52 (t, $^3J_{H\text{-}H}$ = 5.4 Hz, 1H), 4.40 (t, $^3J_{H\text{-}H}$ = 5.2 Hz, 1H), 3.76 – 3.66 (m, 3H), 3.54 (d, $^3J_{H\text{-}H}$ = 5.2 Hz, 2H), 3.42 (m, 2H), 3.13 (d, $^3J_{H\text{-}H}$ = 5.2 Hz, 2H), 2.83 (s, 1H), 2.76 (s, 1H), 2.16 (ddd, $^3J_{H\text{-}H}$ = 12.8, 8.5, 4.0 Hz, 1H), 1.72 (ddd, $^3J_{H\text{-}H}$ = 12.8, 9.3, 3.8 Hz, 1H), 1.30 – 1.14 (m, 2H), 0.72 (ddd, $^3J_{H\text{-}H}$ = 11.9, 4.1, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 137.26 (s, CH), 132.58 (s, CH), 105.41 (s, CH), 68.64 (s, CH_2), 68.46 (s, CH_2), 61.02 (s, CH_2), 59.57 (s, CH_2), 48.71 (s, CH_2), 43.19 (s, CH), 43.11 (s, CH), 41.62 (s, CH), 28.21 (s, CH_2).

General synthesis of TPEUs from pentaerythritol-derived extenders

TPEU synthesis described is based on the synthesis of a polyester-urethane with a 30% hard-block composition using the C_{Nb} extender. Mole ratios calculated using equation S1.

In a clean and dry vial fitted with a magnetic stirrer bar, poly(caprolactone) with a M_w = 2,000 g·mol^{-1} (PCL_{2k}) (1 g, 5 × 10^{-1} mmol) and DBU (3.73 µL, 6.9 × 10^{-3} mmol) were heated to 100 °C under a flow of N_2 for 20 min to aid the reduction of water within the system. The molten mixture was cooled to 80 °C before the addition of H_{12}MDI (359 µL, 1.47 mmol). The reaction mixture was allowed to stir under N_2 for 40 min to allow for prepolymer formation before the addition of a solution of C_{Nb} extender (232 mg, 9.65 × 10^{-1} mmol) dissolved in 100 µL of DMSO. The polymerisation was allowed to proceed for 2h before being removed from the heat to retard further reaction. Any unreacted isocyanate was quenched by washing the TPEU in 50 mL of methanol before being dried *in vacuo*. The molecular weight was analysed *via* GPC analysis. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.97 (m), 5.99 (m), 4.34 – 2.97 (m), 2.89 – 0.50 (m). M_w = 99.0 kg·mol^{-1}, $Đ_M$ = 2.19 (RI detection, DMF GPC).

Functionalisation of C_{Nb}-based TPEUs

TEG-azide In a clean dry vial fitted with a stirrer bar, 30C_{Nb} (1.5 g, 1.5 × 10^{-2} mmol) was dissolved in 1 mL of DMSO. TEG-azide (223 µL, 9.65 × 10^{-1} mmol) was added to the solution before being sealed and heated at 90 °C for 12 hours. The functionalised polymer was recovered by precipitation into cold methanol before being filtered and dried *in vacuo*.

1-thioglycerol In a clean dry vial fitted with a stirrer bar, 30C_{Nb} (1.5 g, 1.50 × 10^{-2} mmol) was dissolved in 1 mL of DMSO. Thioglycerol (104 mg, 9.65 × 10^{-1} mmol) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator (247 mg, 9.63 × 10^{-1} mmol) were added to the solution before being sealed and UV irradiated for 30 min. The functionalised polymer was recovered by precipitation into cold methanol before being filtered and dried *in vacuo*.

7-mercapto-4-methylcoumarin In a clean dry vial fitted with a stirrer bar, 30C_{Nb} (1.5 g, 1.5 × 10^{-2} mmol) was dissolved in 1 mL of DMSO. 7-mercapto-4-methylcoumarin (186 mg, 9.63 × 10^{-1} mmol) and DMPA photoinitiator (247 mg, 9.63 × 10^{-1} mmol) were added to the solution before being sealed and UV irradiated for 30 min. The functionalised polymer was recovered by precipitation into cold methanol before being filtered and dried *in vacuo*.

Wide angle x-ray diffraction (WAXD)

Wide angle x-ray diffraction data was obtained using a Panalytical X'Pert Pro MPD equipped with a Cu Kα_1 hybrid monochromator (λ = 0.154 nm) as the incident beam optics and PiXcel detector was processed using OriginPro 8 software. All UV irradiation was conducted using a Primotech Metalight Classic UV box equipped with a twelve UV light 360° array (ultimate light power within the spectrum of 320-400nm). Each polymer was compression moulded into discs and allowed to anneal for 5 days in an incubator at 25 °C before standard "powder" 2θ-θ diffraction scans were carried out at room temperature in the angular range between 5° and 60° 2θ.

Tensile analysis

Tensile data was obtained at ambient temperature by axially loading 'dog-bones' in a Tensiometric M100-1CT system with a load cell capacity of 1 kN and crosshead speed of 5 mm·min^{-1} with a premeasured grip-to-grip separation. All values reported were obtained from an average of 10 repeat specimens and the results were recorded using winTest v4.3.2 software. Molten polymer samples were moulded into 'dog-bones' *via* compression moulding using a PTFE mould and allowed to cool to ambient temperature before being annealed at 25 °C in an incubator for 5 days.

Static contact angle measurements

Static contact angle measurements were obtained using a KRUSS DSA10 drop shape analyser and were processed using the software package DSA3 1.72b IEEE1394b. Each polymer was dissolved in minimal DMSO before being deposited as a thin film on a glass slide. The solvent was allowed to evaporate overnight before trace solvent was removed *in vacuo*. TPEU samples were allowed to anneal at 25 °C in an incubator for 5 days prior to analysis. Using a KRUSS DSA100 a 100 µL droplet of DI H_2O was deposited onto the surface of the film and the measurement was taken immediately and analysed using a sessile drop type with a polynomial (tangent 2) computational method.

Degradation study

Accelerated degradation studies were conducted under conditions previously reported by C X F Lam *et al.*[4] All polymers which could form 'degradation disks' were subjected to accelerated degradation studies (5M aq. NaOH). Molten polymer samples were moulded into disks *via* compression moulding at 200 °C using a PTFE mould and allowed to cool to ambient temperature. The disks were placed in individual vials containing 20 mL of 5M NaOH solution and incubated at 37 °C. with constant agitation at 60 rpm. The surface of the disks were 'dab'-dried using KIMTECH SCIENCETM precision wipes in order to remove excess surface water before the weight was measured periodically using an analytical balance.

Determination of mole ratios with varying %HS

Equation S1;

$$\%HS = \frac{100(R-1)(M_{ex}+M_{di})}{(M_{po}+R(M_{di})+(R-1)(M_{ex})} \qquad (S1)$$

Where, M_{ex}, M_{di} and M_{po} are the mole average molecular weights of the extender, diisocyanates and polyol respectively and R is the mole ratio of the diisocyanates to the polyol. TPEUs with a varying %HS of 30, 45 and 60% were selected and the mole ratio of diisocyanate to polyol was calculated by solving for R (Table 1).

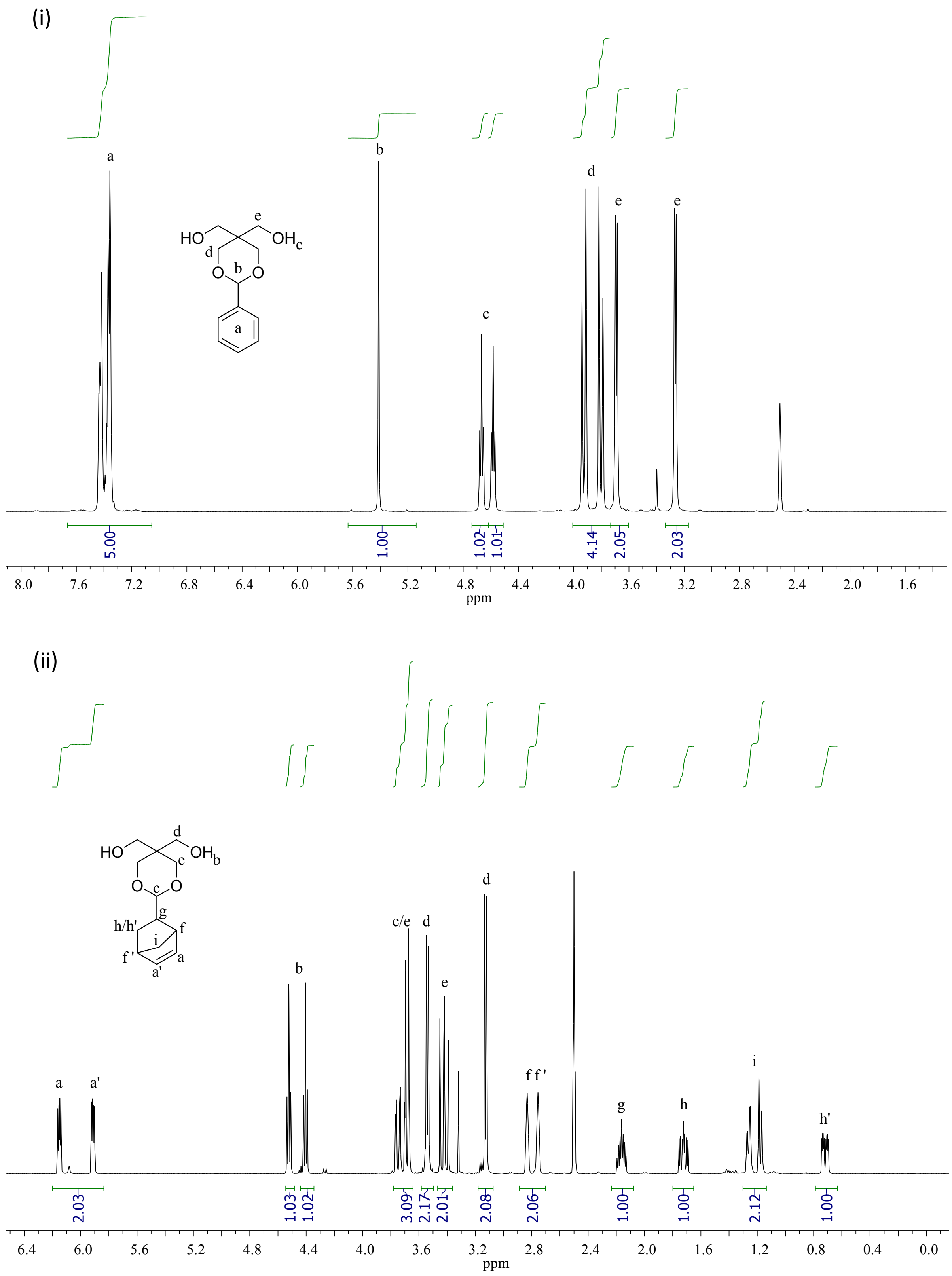

Figure S1. ^{1}H NMR spectra of (i) (2-phenyl-1,3-dioxane-5,5-diyl)dimethanol (C_{Ph}) and (ii) 2-(norbornene)-1,3-dioxane-5,5-diyl)dimethanol (C_{Nb}) (400 MHz, 298 K, DMSO-d6).

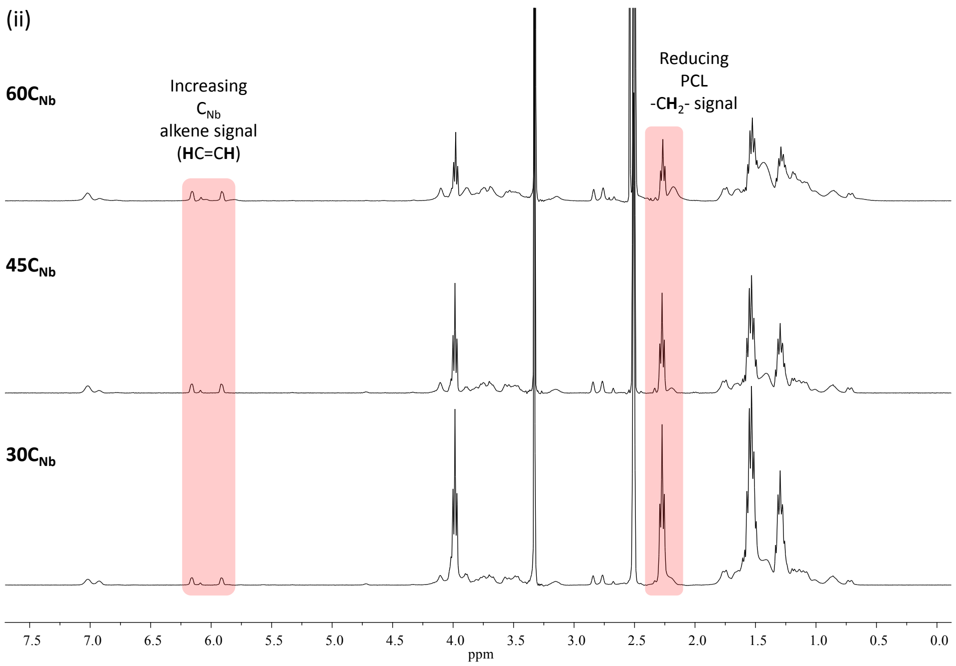

Figure S2. ^{1}H NMR spectra of (i) C_{Ph}-based TPEUs and (ii) C_{Nb}-based TPEUs (400 MHz, 298 K, DMSO-*d*$_6$).

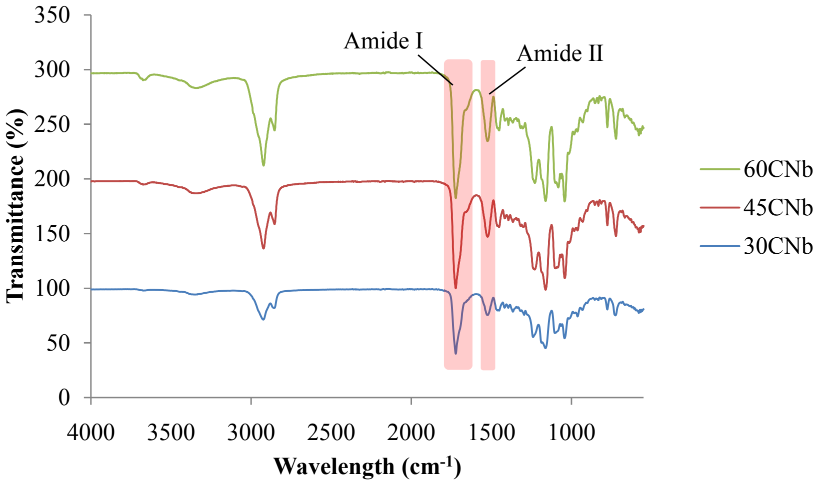

Figure S3. FT-IR spectra of C_{Nb}-based TPEUs.

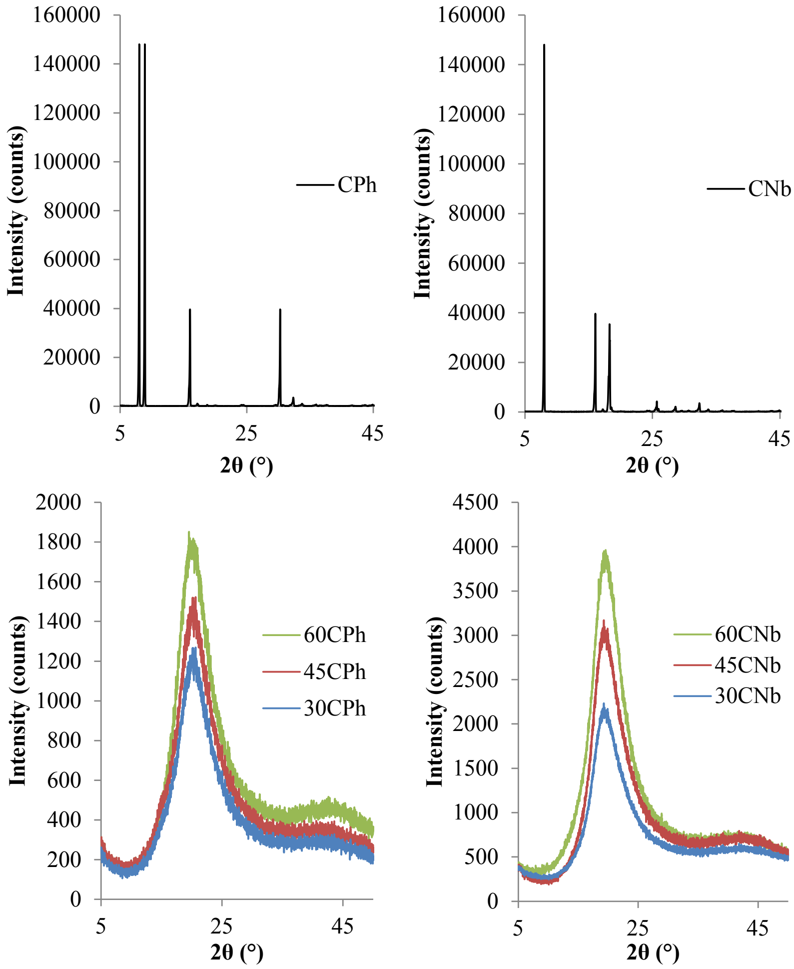

Figure S4. WAXD diffractograms of C_{Ph} extender and resultant TPEUs. C_{Nb} extender and resultant TPEUs.

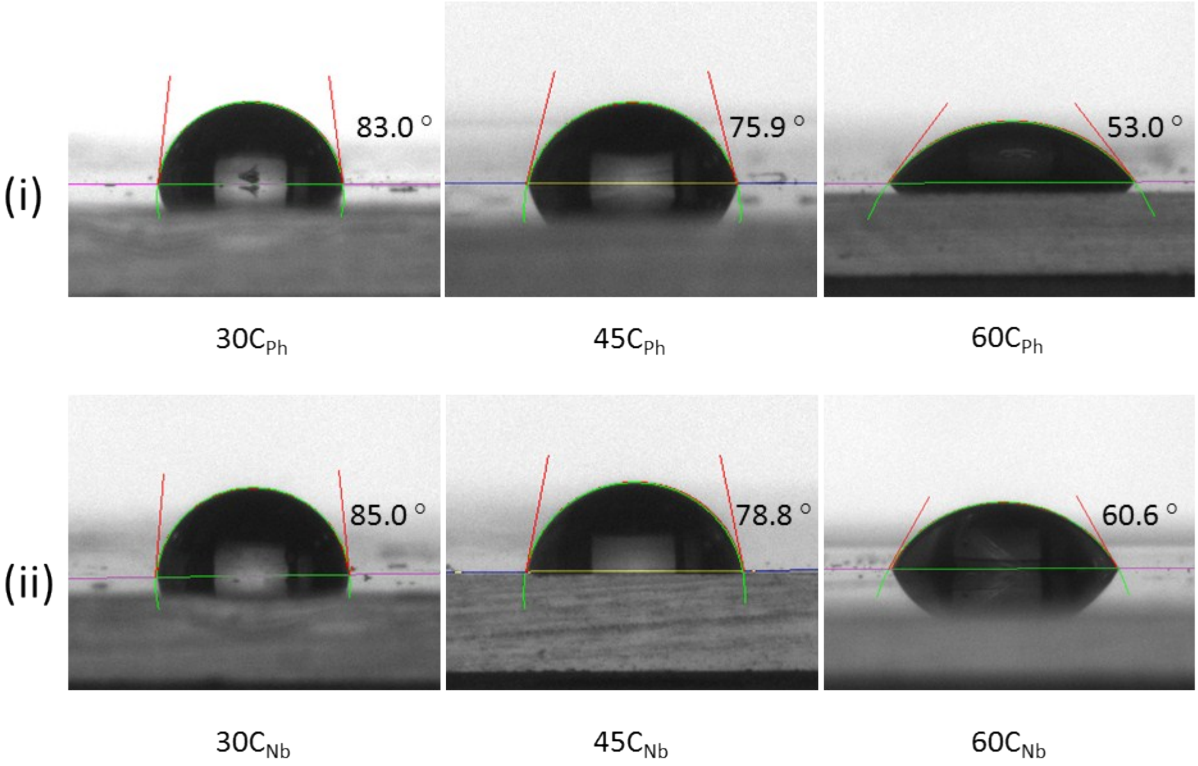

Figure S5. Static contact angle measurements for (i) C_{Ph} and (ii) C_{Nb}-based TPEUs.

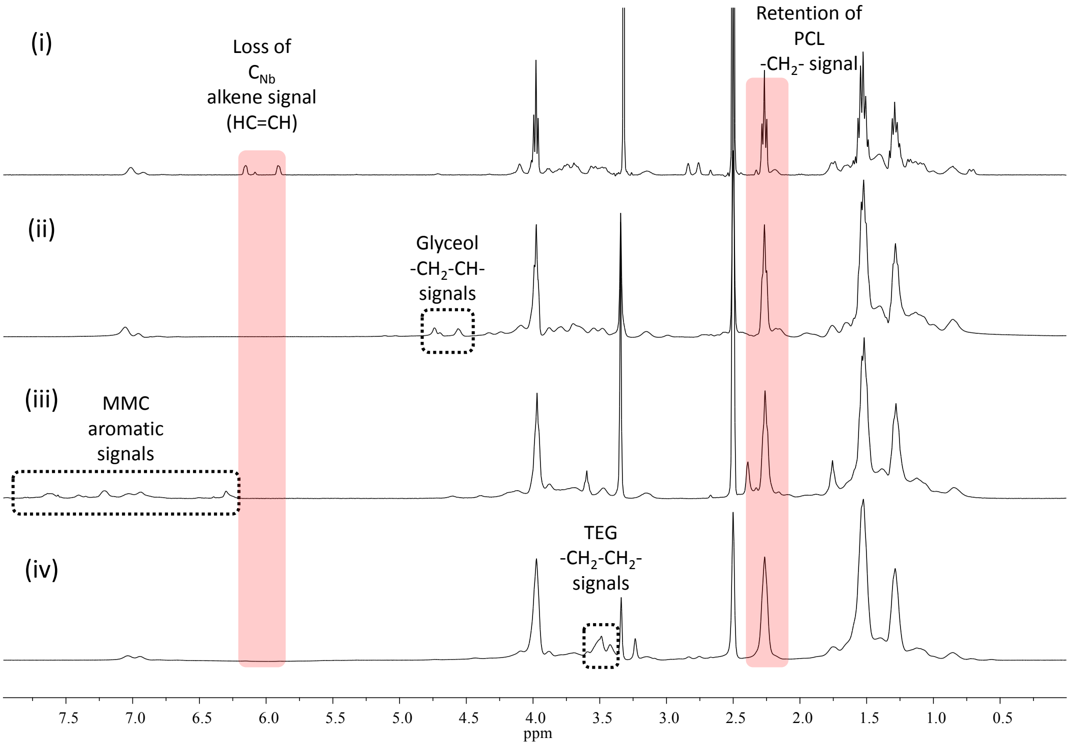

Figure S6. ^{1}H NMR spectra of (i) $45C_{Nb}$, (ii) $45C_{Nb}$-gly, (iii) $45C_{Nb}$-MMC and (iv) $45C_{Nb}$-TEG TPEUs (400 MHz, 298 K, DMSO-d_6).

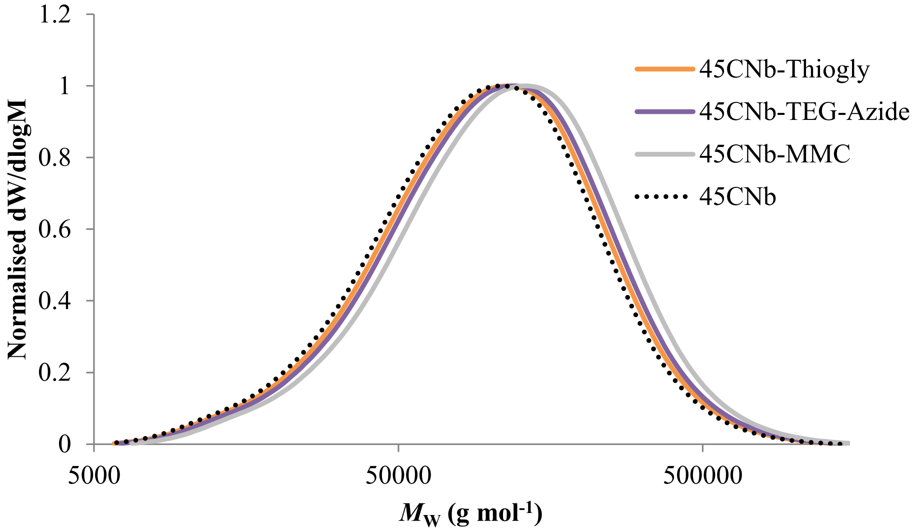

Figure S7. Size exclusion chromatograms of modified 45C$_{Nb}$-based TPEUs in DMF against PMMA standards.

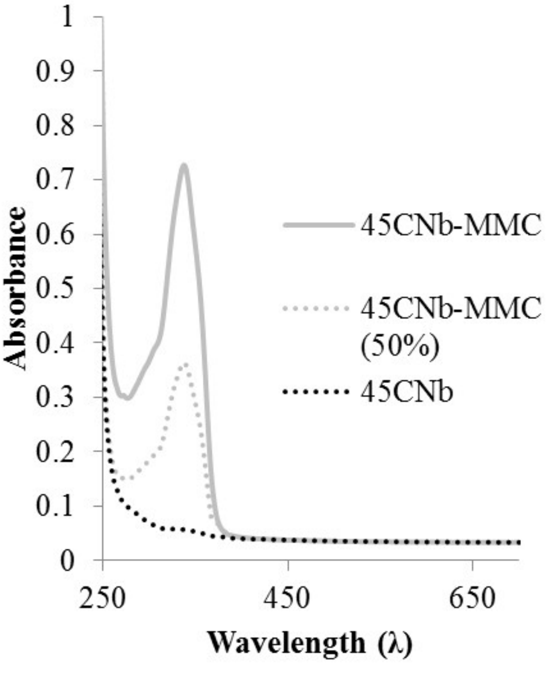

Figure S8. 45C$_{Nb}$-MMC TPEUs; UV-Vis absorption spectra at varying percentage modification.

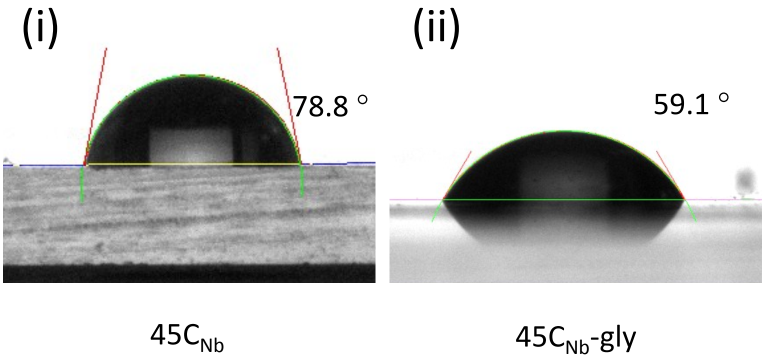

Figure S9. Static contact angle measurements for (i) $45C_{Nb}$-based and (ii) 45 C_{Nb}-gly TPEUs.

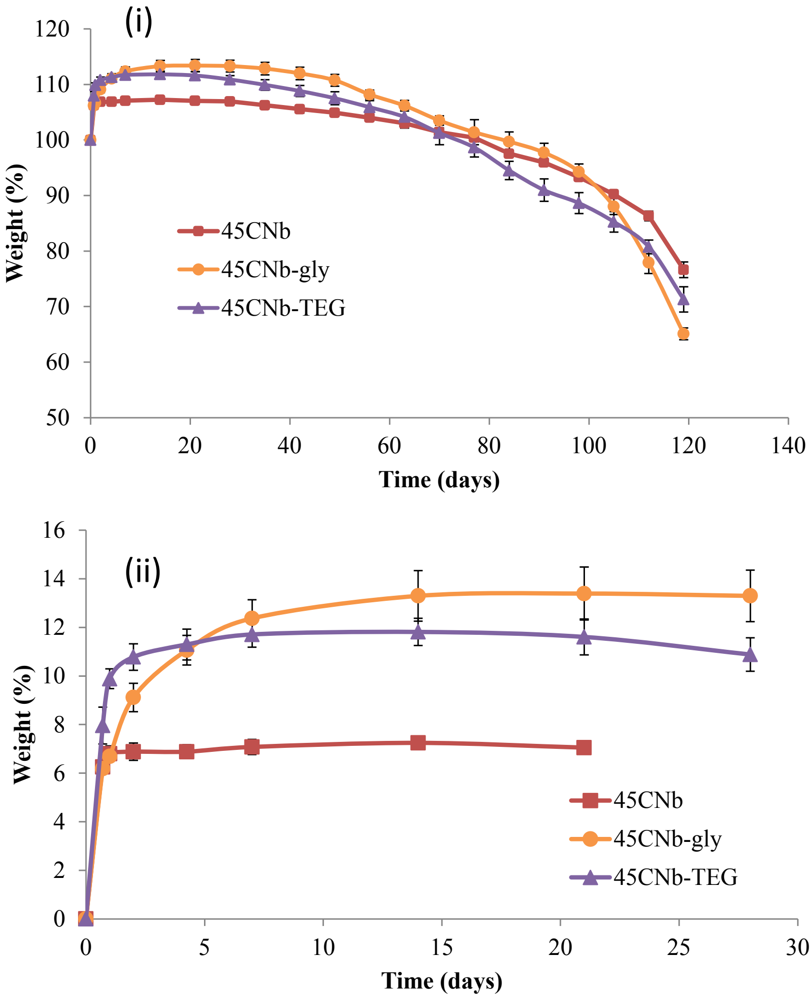

Figure S10. Percentage (i) degradation and (ii) swelling for modified $45C_{Nb}$-based TPEUs, average of 3 samples.

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2. J. Xu, Z.-L. Liu and R.-X. Zhuo, *J. Appl. Polym. Sci.*, 2006, **101**, 1988-1994.
3. M. C. Arno, R. P. Brannigan, G. M. Policastro, M. L. Becker and A. P. Dove, *Biomacromolecules*, 2018, **19**, 3427-3434.
4. C. X. Lam, M. M. Savalani, S. H. Teoh and D. W. Hutmacher, *Biomed Mater*, 2008, **3**, 034108.