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DOI:
[10.1039/C9PY00951E](https://doi.org/10.1039/C9PY00951E)

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Document Version
Publisher's PDF, also known as Version of record

Citation for published version (Harvard):
Brannigan, RP, Walder, A & Dove, A 2019, 'Application of functional diols derived from pentaerythritol as chain extenders in the synthesis of novel thermoplastic polyester-urethane elastomers', *Polymer Chemistry*, vol. 10, no. 38, pp. 5236-5241. <https://doi.org/10.1039/C9PY00951E>

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

Ruairi P. Brannigan,^a Anthony Walder^c and Andrew P. Dove^{b,d}

The success of thermoplastic elastomers is owed to the wide range of thermal, mechanical and degradation properties that enable them to be tuned to myriad applications. In large, this is achieved through the manipulation of the chemical structure of their component parts e.g. polyol, diisocyanate and diol chain extender. The permutation of diol extenders is of great interest industrially owing to their commercial availability and ease of synthesis and purification, however, the incorporation of extenders with post-polymerisation modifiable sites, specifically moieties prone to 'click' coupling chemistries has been relatively overlooked until recent times. Herein, the application of 'acetal-diols', (2-phenyl-1,3-dioxane-5,5-diyl)dimethanol (C_{Ph}) and (2-(norbornene)-1,3-dioxane-5,5-diyl)dimethanol (C_{NB}), as extenders in the synthesis of novel thermoplastic polyurethanes (TPUs) is described. The assessment of their structure–property relationship reveals that the material properties are highly tailorable based on their urethane content. Furthermore, norbornene 'click' chemistries could be utilised post-polymerisation as a method of manipulating the materials' hydrophilicity and degradability.

Received 28th June 2019,
Accepted 6th September 2019

DOI: 10.1039/c9py00951e

rsc.li/polymers

Introduction

Characterised by their enhanced ability to recover after incurring high strains and deformation, thermoplastic elastomeric materials have been of great interest in both biomedical and wider industrial applications.^{1–3} Of this class of materials, thermoplastic polyurethanes (TPUs) are arguably the most widely investigated and utilised. This category of segmented elastomeric polymers is generally synthesised *via* the step-growth polymerisation of telechelic polymeric diols (polyols) with diisocyanates and small diol 'chain-extendors', however, more recently analogues of these systems have been synthesised through the ring-opening polymerisation of cyclic carbonates.^{4–7} The success of elastomeric TPUs is owed to their ability to access a vast range of thermal and mechanical properties through the mediation of their component parts.

Most notable of these is the incorporation of hydroxyl terminated telechelic polyesters (*i.e.* poly(ϵ -caprolactone) (PCL), poly(lactide-*co*-glycolide) (PLGA), poly(trimethylene carbonate) (PTMC) *etc.*) as the polyol, yielding hydrolytically degradable thermoplastic polyester urethanes (TPEUs).^{8–10} Equally, the permutation of diol extenders is of great interest industrially owing to their commercial availability and ease of synthesis and purification. The design of novel small diol extenders in order to control the physical properties of the resultant TPEUs has been extensively investigated since their inception, however, the application of extenders with post-polymerisation modifiable sites has been relatively overlooked until recent times.^{11,12}

So-called 'click' reactions have been extensively utilised in polymer chemistry as an efficient method for the conjugation of target molecules onto polymeric constructs.^{13–15} Although initially outlined under criteria set out by Kolb, Finn and Sharpless, the definitive qualities of 'click' reactions have been modified since their application in polymer chemistry.¹⁶ In relation to polymer chemistry, 'click' reactions must be equimolar, allow for facile large scale purification, proceed in a rapid manner, be high yielding and utilise stable products.¹⁶ One moiety which has been extensively studied, owing to its ability to undergo a selection of 'click' reactions, is norbornene. Norbornene moieties can efficiently undergo 1,3-dipolar cycloaddition with azides, inverse electron-demand Diels–Alder (DA_{inv}) reactions with tetrazines and photoinduced

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†Electronic supplementary information (ESI) available. See DOI: 10.1039/c9py00951e



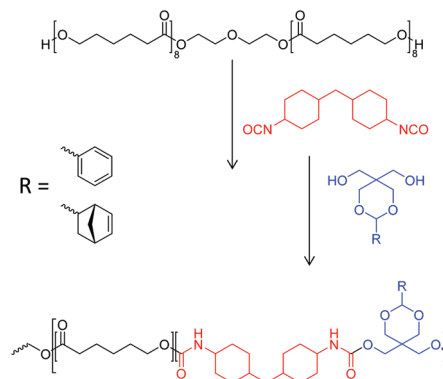
radical thiol addition reactions in addition to several non-'click' conjugation methods.^{17–22}

The incorporation of cyclic acetal moieties into polymeric systems represents a very important advancement in the development of biocompatible, hydrolytically degradable and pH responsive materials.^{23–25} Cyclic acetals are therefore excellent candidates in the synthesis of pH responsive drug delivery vectors. Recently, we have shown that the incorporation of norbornene-acetal moieties in an amphiphilic polycarbonate-g-poly(ethylene glycol) system yielded materials which could be easily modified through 'click'-like chemistry and subsequently used as a pH responsive chemotherapeutic delivery system.²⁶ Herein, we describe the application of previously synthesised 'acetal-diols', (2-phenyl-1,3-dioxane-5,5-diyl)dimethanol (C_{Ph}) and (2-(norbornene)-1,3-dioxane-5,5-diyl)dimethanol (C_{Nb}), as extenders in the synthesis of novel TPEUs and assess their structure–property relationship. Furthermore, the post-polymerisation modification of the norbornene-containing TPEUs, as a method of manipulating their physical properties, is investigated.

Results and discussion

As has been previously reported, the acid-catalysed acetal formation between aldehydes and diols offers a facile and efficient route to synthesise monomers and polymers that contain pH sensitive cyclic acetal moieties.^{26,27} Acetal-containing diols were generated through the reaction of pentaerythritol with benzaldehyde and norbornene-2-carboxaldehyde under acidic conditions respectively. The utilisation of deionised water as the reaction solvent allowed for the precipitation of the mono-functionalised product from the reaction exclusively (Fig. S1†), owing to the increased hydrophobicity of the molecule through the introduction of the benzyl and norbornene moieties. The conversion of pentaerythritol to the benzylidene acetal functional diol (C_{Ph}) was confirmed by 1H and ^{13}C NMR spectroscopy. From the 1H NMR spectrum, the evolution of a multiplet at $\delta = 7.45$ – 7.31 ppm and a singlet at $\delta = 5.40$ ppm, attributed to the benzyl functionality and the methine adjacent to the acetal respectively, verify the successful modification of the pentaerythritol. This is further confirmed by the presence of two triplets at $\delta = 4.57$ and 4.66 ppm attributed to the protons of the diol hydroxyl groups (Scheme 1). Similarly, the synthesis of (2-(norbornene)-1,3-dioxane-5,5-diyl)dimethanol (C_{Nb}) was also verified by 1H and ^{13}C NMR spectroscopy through the presence of a series of signals between $\delta = 3.00$ ppm and 0.60 ppm, attributed to the saturated norbornene hydrocarbons (Fig. S1†).

Furthermore, the presence of two multiplets at $\delta = 6.17$ ppm and 5.94 ppm confirms the retention of the norbornene alkene functionality (Fig. S1†). As has been previously reported, the most utilised method in the synthesis of TPUs is the '2-shot' method, owing to the formation of highly segmented thermoplastic polyester urethanes (TPEUs).^{28,29} This method involves the formation of a polyester-based 'pre-



Scheme 1 Synthesis of cyclic acetal containing (TPEUs) via a '2-shot' method.

polymer' by the reaction of the polyol with an excess of diisocyanates. This yields isocyanate end-capped polyesters which are subsequently polymerised by step-growth methods by the addition of a small diol extender. Hydroxy-terminated telechelic poly(ϵ -caprolactone) with a weight-average molecular weight (M_w) = 2000 g mol^{-1} (PCL_{2k}), as determined by size exclusion chromatography (SEC), was selected as the polyol and 1-isocyanato-4-[(4-isocyanatocyclohexyl)methyl] cyclohexane (H_{12} MDI) was chosen as the diisocyanate. The weight percentage of the overall TPEU that is 'hard segment' (%HS) was determined based on the overall urethane content, and TPEUs with varying target %HS of 30, 45 and 60% were synthesised. The molar ratio of diisocyanate to polyol was calculated using eqn (S1).[†] By altering the composition of the TPEUs by varying the %HS and extender used, it is possible to tune the morphology of these segmented materials and in turn the mechanical properties.³⁰ In addition, owing to its relatively low toxicity in comparison to conventional tin-based catalysts, 1,8-diazabicycloundec-7-ene (DBU) was employed as an organocatalyst for the step-growth polymerisation through the activation of the polyol/extender hydroxyl groups, aiding in the nucleophilic attack of the isocyanate bonds. The polymerisation was monitored by Fourier-transform infra-red (FT-IR) spectroscopy through the reduction of absorption bands attributed to the cumulated double bonds of the diisocyanate at $\sim 2275 \text{ cm}^{-1}$ and $\sim 2250 \text{ cm}^{-1}$. Furthermore, it is inferred the complete consumption of the diisocyanate is indicative of full incorporation of the diol chain extender. SEC analysis revealed that the C_{Ph} and C_{Nb} -based TPEUs exhibited unimodal weight distributions with dispersities (D_M) close to 2 ($D_M \approx 2.1$ – 2.4), characteristic of step growth polymerisations (Table 1 and Fig. 1).³¹ Interestingly, it was noted that the dispersities of the TPEUs increased, while the M_w decreased, with increasing %HS. It is hypothesised that this is a consequence of the increased viscosity of the polymerisation reaction with higher molar ratios of diisocyanate/extender to polyol, reducing the availability of reactive chain ends.

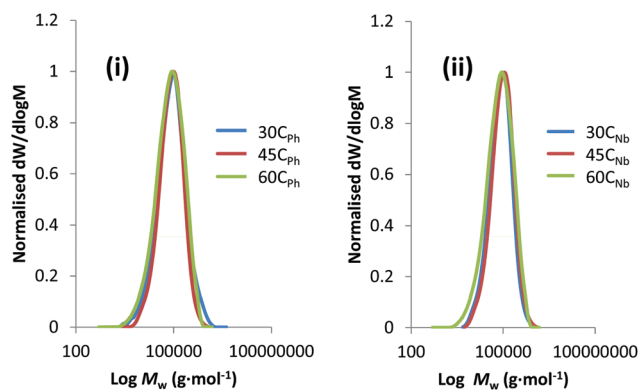
The final composition of the C_{Ph} and C_{Nb} -based TPEUs, as calculated by eqn (S1),[†] were verified by 1H NMR and FT-IR



Table 1 Composition and molecular weight comparison of C_{Ph} and C_{Nb}-based TPEUs

Polymer	wt% 'hard block' (%HS)	H ₁₂ MDI/polyol ratio ^a (<i>R</i>)	<i>M_w</i> ^b (kg mol ⁻¹)	<i>D_M</i> ^b
30C _{Ph}	30	2.99	97.8	2.18
45C _{Ph}	45	4.80	97.0	2.23
60C _{Ph}	60	7.97	88.5	2.30
30C _{Nb}	30	2.93	99.0	2.19
45C _{Nb}	45	4.68	108.9	2.17
60C _{Nb}	60	7.75	90.1	2.38

^a Determined by eqn (S1). [†] ^b Determined by GPC analysis in DMF against poly(methyl methacrylate) (PMMA) standards.

**Fig. 1** Size exclusion chromatograms of (i) C_{Ph} and (ii) C_{Nb}-based TPEUs in DMF against PMMA standards (Table 1).

spectroscopy. Expectedly, it was found by ¹H NMR spectroscopy, for both C_{Ph} and C_{Nb}-based materials, that the signals attributed to the PCL 'soft' block ($\delta = 3.98, 2.27, 1.52$ and 1.29 ppm) decreased with increasing %HS. In conjunction with this, the characteristic signals attributed to the functionalised pentaerythritol-derived extenders (C_{Ph}; $\delta = 7.36$ and 5.45 ppm, $\delta =$ C_{Nb}; 6.30 – 5.80 ppm) were found to increase proportionally with increasing %HS, indicative of good extender incorporation into the final materials (Fig. S2[†]). Furthermore, the FT-IR spectra of both the C_{Ph} and C_{Nb}-based TPEUs displayed absorption bands attributed to the urethane carbonyl stretching (amide I) and N–H bending (amide II) frequencies at ~ 1700 and ~ 1500 cm⁻¹ respectively. Analogous to the trend observed in the ¹H NMR spectra, it was found that these absorptions increased proportionally to the %HS. Importantly, it was noted that the absence of an absorbance band between 2250 and 2275 cm⁻¹, attributed to the isocyanate cumulative double bonds, is indicative of complete consumption of the H₁₂MDI (Fig. S3[†]). Owing to differences in scattering patterns of contrasting polymers in segmented block copolymer systems, wide angle X-ray diffraction (WAXD) analysis can be used to determine phase separation within a material.^{32–34}

As such, in order to assess the morphology of the materials and verify the synthesis segmented TPEUs, annealed materials were subjected to WAXD analysis. For both C_{Ph} and C_{Nb} extenders, it was found that the X-ray diffraction patterns displayed

a series of sharp crystalline peaks with a Bragg's angle (2θ) between 5 – 30° , however, the resultant TPEUs were found to display two broad undefined peaks at $2\theta \approx 20^\circ$ and $2\theta \approx 44^\circ$. This is indicative of phase separated amorphous domains attributed to the 'hard' polyurethane segment and the 'soft' PCL segment respectively.^{35,36} (Fig. S4[†]).

In order to assess the tensile properties of the C_{Ph} and C_{Nb}-based TPEUs in relation to their composition, annealed materials with varying %HS were subjected to axial loading at a constant crosshead speed (5 mm min⁻¹) until failure. From an average of 10 comparable samples, the Young's modulus (E), elongation at break (ϵ_{break}) and ultimate tensile strength (UTS) of the materials were determined (Table 2). The tensile analysis of the TPEUs expectedly displayed that both UTS and E increased proportionately with %HS, however, ϵ_{break} was found to be inversely proportional. As is evident from previous synonymous studies, this is a consequence of increased hydrogen bonding through the urethane moieties of the 'hard' segments, yielding brittle materials. It was noted that both the C_{Ph} and C_{Nb}-based TPEUs with a 45% 'hard-block' content (45C_{Ph} and 45C_{Nb}, Table 2), displayed non-linear viscoelastic behaviour with relatively good elongation before mechanical failure (420 – 460% strain) and underwent recoverable deformation at 30 – 40% strain. Furthermore, at high %HS (60%) it was found that TPEUs underwent plastic deformation and mechanical failure at low strains ($<45\%$) but exhibited a high UTS (>29 MPa).

Conversely to this, at lower %HS (30%), TPEUs were found to have high elongation before mechanical failure (760 – 1130% strain) but exhibited extended recovery times after undergoing elastic deformation with low E (5 – 8 MPa) and UTS (2 – 6 MPa) (Fig. 2). C_{Ph} and C_{Nb}-based TPEUs were subjected to accelerated degradation conditions in order to assess their hydrolytic degradability. Each of the TPEUs were compression moulded into degradation 'disks' and placed into individual vials before being submerged in basic aqueous media (5 M aq. NaOH). The degradation samples were stored at 37 °C with constant agitation at 60 rpm and the weights of the dried disks were measured periodically with an analytical balance until they were irretrievable from the degradation media. This method was chosen to exhibit the hydrolytic degradation of the TPEUs as it allowed for the most rapid analysis and comparison of the degradation properties of the materials. The accelerated degradation was performed in triplicate and all

Table 2 Comparison of tensile properties of C_{Ph} and C_{Nb}-based TPEUs

Polymer	E^a (MPa)	$\epsilon_{\text{break}}^a$ (%)	UTS ^a (MPa)
30C _{Ph}	8.4 ± 1.4	757 ± 10	5.9 ± 0.16
45C _{Ph}	39.6 ± 2.8	424 ± 9	24.4 ± 0.44
60C _{Ph}	109.8 ± 5.6	41 ± 3	29.6 ± 1.01
30C _{Nb}	4.6 ± 0.9	1130 ± 19	2.2 ± 0.26
45C _{Nb}	40.2 ± 2.0	462 ± 12	25.3 ± 0.86
60C _{Nb}	110.3 ± 6.8	47 ± 2	30.5 ± 1.30

^a Determined by tensiometric analysis (average of 10 samples, Fig. 2).



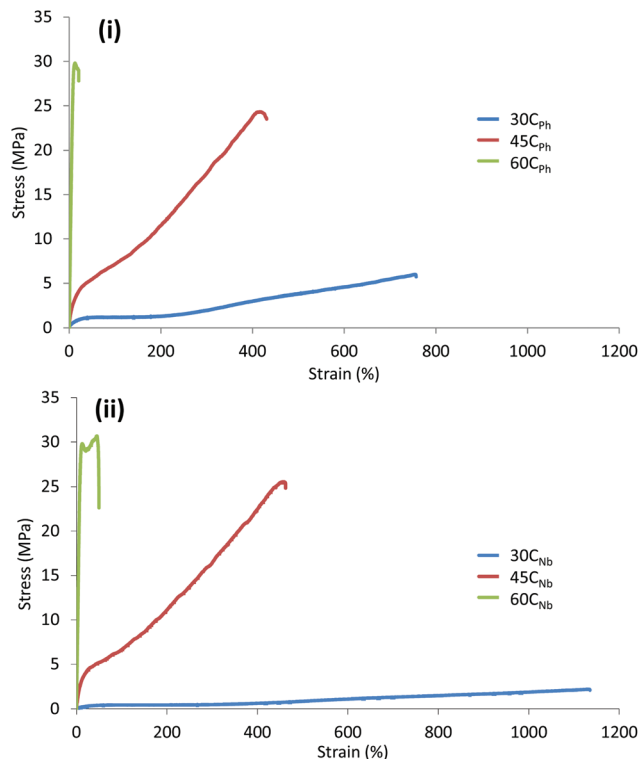


Fig. 2 Exemplar stress–strain curves of (i) C_{Ph} -based TPEUs and (ii) C_{Nb} -based TPEUs. Experiments were conducted at ambient temperature ($\sim 25\text{ }^{\circ}\text{C}$) at an elongation rate of 5 mm min^{-1} until failure.

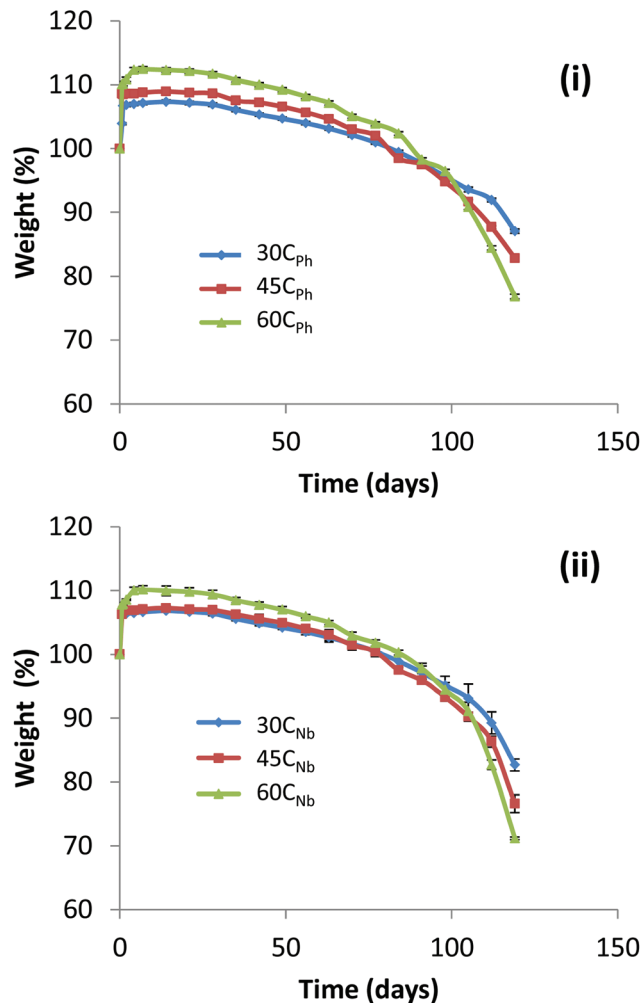
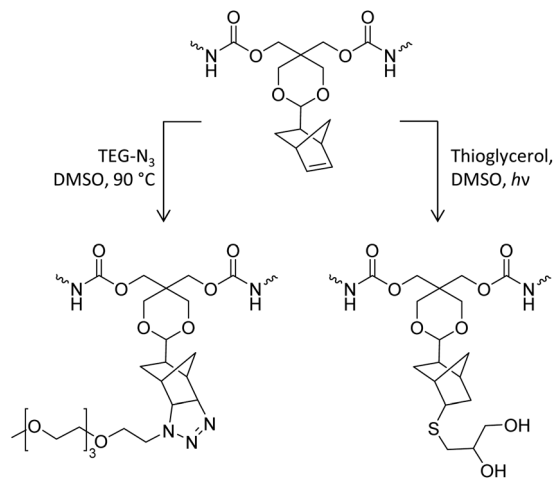


Fig. 3 Hydrolytic degradation of (i) C_{Ph} and (ii) C_{Nb} -based TPEUs under accelerated degradation conditions. Percentage mass loss of an average of three samples.

results were reported as an average. For both C_{Ph} and C_{Nb} -based TPEUs, it was noted that differences in the overall percentage swelling and rate of degradation observed were found to be negligible, irrespective of the side group functionality (maximum swelling $60C_{Ph} = 14 \pm 0.6\%$, $60C_{Nb} = 11 \pm 0.8\%$, Fig. 3). Furthermore, it was found that the percentage swelling increased slightly with increasing %HS. It is hypothesised that this is owing to the decrease in the hydrophobic PCL domains, generating a more hydrophilic material. In order to verify this hypothesis, static contact angle measurements with water were conducted on thin films of the TPEUs. The contact angle of a material is defined as the angle of a liquid/vapour interface when in contact with a solid surface. This angle can therefore be used to infer the relative hydrophilicity/hydrophobicity of a surface owing to differences in the interfacial tension caused by the surface composition. If the contact angle is greater than 90° the surface is said to be non-wetting (hydrophobic), whereas a contact angle of less than 90° denotes a surface which is said to be wettable (hydrophilic) with an angle of 0° which indicates complete wetting.¹² Concurrent with the accelerated degradation study, it was found that the difference in contact angle measurements were relatively low when side-group functionality was changed from phenyl to norbornene acetal (Fig. S5[†]). Moreover, the contact angle measurements verified the increase in hydrophilicity with increasing %HS hypothesised in the accelerated degradation study (Scheme 2).

As has been demonstrated in the literature, the post-polymerisation modification of norbornene-containing polymers offers a unique method of creating novel materials with various properties and applications.²² As such, in order to assess the effect the modification of C_{Nb} -based TPEUs with hydrophilic small molecules has on the overall hydrophilicity and degradation profile of the TPEUs, C_{Nb} -based TPEUs were modified *via* a 1,3-dipolar cycloaddition with *O*-(2-azidoethyl)-*O'*-methyl-triethylene glycol (TEG-azide) and the photoinduced radical thiol addition with 1-thioglycerol. Furthermore, C_{Nb} -based TPEUs were modified with the fluorophore, 7-mercapto-4-methylcoumarin (MMC), in order to demonstrate the efficiency of the modification process *via* ultraviolet-visible (UV-Vis) spectrophotometry. The ^1H NMR spectra of the modified C_{Nb} -based TPEUs reveal the complete consumption of the norbornene alkene functionality at $\delta = 5.94$ and 6.17 ppm and the appearance of characteristic signals attributed to each modification (TEG-azide; $\delta = 3.50$ ppm, 1-thioglycerol; $\delta = 4.50$ – 5.00 ppm, 7-mercapto-4-methylcoumarin; 7.75 – 6.75 and





Scheme 2 The post-polymerisation functionalisation of the norbornene acetal moieties of C_{Nb} -based TPEUs.

7.20 ppm, Fig. S6†), indicative of successful post-polymerisation modification. The modified TPEUs were analysed by GPC and were found to increase in molecular weight with no significant effect on the dispersities, indicative of no adverse side reactions *i.e.* chain–chain coupling, side-group cleavage *etc.* (Fig. S7†). Additionally, the successful modification of $45C_{Nb}$ with the fluorophore MMC ($45C_{Nb}$ -MMC) was also verified by UV-vis spectrophotometry. It was found that the unmodified $45C_{Nb}$ exhibited no absorbance peak, however, after modification, a peak at $\lambda = 388$ nm was observed characteristic of the absorbance of 7-mercapto-4-methylcoumarin. Furthermore, it was noted that by reducing the equivalents of MMC used during the photoinduced thiol addition (1.1 eq. to 0.51 eq.) it was possible to control the incorporation of fluorophore into the molecule. This was denoted by a reduction in the intensity of absorbance observed, in accordance with the Beer–Lambert law (Fig. S8†).

In order to assess the effect that the modification of C_{Nb} -based TPEUs with hydrophilic small molecules has on the swelling/degradation profiles and surface hydrophilicity, thioglycerol ($45C_{Nb}$ -gly) and *O*-(2-azidoethyl)-*O'*-methyl-triethylene glycol ($45C_{Nb}$ -TEG) modified TPEUs were subjected to accelerated degradation studies and static contact angle measurements as previously described. As anticipated, the incorporation of hydrophilic molecules into the ‘hard’ polyurethane segments led to an increase in the surface hydrophilicity of the materials observable by a severe reduction in the static contact angle measurements from 78.8° to 59.1° (Fig. S9†). Furthermore, the accelerated degradation study revealed that the percentage swelling of the modified TPEUs increased from 7% to 13% after modification, indicative of an increased ingress of the aqueous degradation media into the TPEU network owed to increased hydrophilicity (Fig. S10†). In conjunction with the increase in percentage swelling, it was noted that a slightly higher rate of weight loss was also observed. The increased rate of weight loss is indicative of a higher hydrolytic

Table 3 Comparison of tensile properties of modified C_{Nb} -based TPEUs

Polymer	E^a (MPa)	ϵ_{break}^a (%)	UTS ^a (MPa)
$45C_{Nb}$	40.2 ± 2.0	462 ± 12	25.3 ± 0.86
$45C_{Nb}$ -Thiogly	37.8 ± 2.7	474 ± 17	24.4 ± 1.33
$45C_{Nb}$ -TEG	32.4 ± 1.8	519 ± 13	22.3 ± 0.98
$45C_{Nb}$ -MMC	6.7 ± 1.8	165 ± 6	2.5 ± 1.10

^a Determined by tensiometric analysis (average of 10 samples).

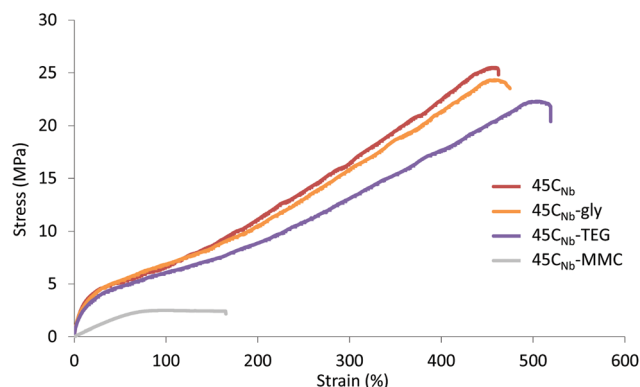


Fig. 4 Exemplar stress–strain curves of modified C_{Nb} -based TPEUs. Experiments were conducted at ambient temperature ($\sim 25^\circ\text{C}$) at an elongation rate of 5 mm min^{-1} until failure.

degradation rate owed to the increased concentration of degradation media at hydrolysable bonds.

Finally, in order to assess the effect the post-polymerisation modifications had on the mechanical properties of the materials, modified $45C_{Nb}$ -based TPEUs were analysed by tensiometric analysis. Furthermore, in order to generate consistent results, all of the modified TPEUs were processed, annealed and analysed under the same conditions. From tensiometric analysis, it was found that there was no significant change in the tensile properties of the $45C_{Nb}$ -gly TPEU in comparison with the unmodified TPEU, whilst the $45C_{Nb}$ -TEG TPEU remained comparable with only minimal reduction in E and UTS. It was noted, however, that there was a significant increase in the ϵ_{break} of the $45C_{Nb}$ -TEG materials attributed to the associative behaviour of the mobile pendant TEG units. Interestingly, it was noted that the $45C_{Nb}$ -MMC polymers exhibited drastic reductions in E , UTS and ϵ_{break} owed to the disruptive nature of the bulky pendant groups on the phase separation of the TPEUs (Table 3 and Fig. 4).

Conclusions

In conclusion, pentaerythritol, through the acid catalysed acetal formation, was shown to be an excellent platform in the synthesis of novel functional thermoplastic polyester-urethanes with a range of mechanical properties determined by extender content. Furthermore, as is evident from the study,



norbornene-functional TPEUs (C_{Nb}) offer a unique route to decorated elastomeric materials which may be employed to control the hydrophilicity and degradation rate of the materials with minimal effect on the mechanical properties through post-polymerisation modifications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Lubrizol Corporation and the University of Warwick are thanked for funding to support the studentship (R. B.).

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