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Functional α,ω-Dienes via Thiol-Michael Chemistry: Synthesis, Oxidative Protection, Acyclic Diene Metathesis (ADMET) Polymerization and Radical Thiol-ene Modification

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The synthesis of the novel α,ω-diene 2-(undec-10-en-1-yl)tridec-12-en-1-yl acrylate is described. Thiol-Michael coupling of this substrate followed by chemoselective oxidation of the thioether moiety with triazotriphosphorine tetrachloride (TAPC) furnished a suite of functional and symmetrical ADMET-active monomers in a quick and convenient manner. Polymerization of these adducts with Grubbs 1st generation catalyst ($RuCl_2(PCy_3)_2CHPh$)was demonstrated to high conversion, and quantitative radical initiated thiol-ene modification of the backbone C=C bonds was performed to impart additional functionality to each ADMET polymer. These reactions highlight the compatibility of thiol-based click chemistries for the preparation and post-modification of functional ADMET materials.

Introduction

Highly efficient conjugation and 'click' reactions have become a central theme of modern polymer research as tools for monomer synthesis, polymer modification as well as for the synthesis of more advanced architectural materials.[1, 2] Chemistries such as the Cu-catalyzed cycloaddition of an alkyne and an azide (CuAAC),[3-8] Diels-Alder reactions,[9-13] oxime chemistry,[14, 15] radical and nucleophilic hydrothiolation of an ene[16-27] or yne,[28-32] thiol-isocyanate,[33] thiol-halo,[34] and reactions with highly activated esters[35-37] are well documented. Of this suite of efficient chemical transformations, the CuAAC is still the preeminent example of a 'click' reaction while the use of thiol-ene and thiol-yne chemistries has increased dramatically in recent years.

Our group has recently been exploring novel ways in which to combine ring-opening metathesis polymerization (ROMP) with thiol-based coupling chemistries,[38] including: the synthesis and (co)polymerization of a series of novel thioether based functional *exo*-7-oxanorbornenes,[39] the preparation of hyperbranched (co)polymers from difunctional *exo*-7-oxanorbornene monomers,[40] the synthesis and polymerization of dendron macromonomers,[41] the quantitative hydrothiolation of a ROMP polymer backbone[42] and the selective thiol-yne modification of alkyne side groups in the presence of internal backbone enes.[43] ROMP is a particularly attractive transition metal-mediated polymerization technique facilitating the preparation of (co)polymers in a controlled fashion with low dispersities and, with modern Grubbs' and Schrock catalysts/initiators, now exhibits a functional group tolerance comparable to that exhibited by reversible deactivation radical polymerization processes.[44-47]

The complementary metathesis-based polymerization process, acyclic diene metathesis (ADMET) polymerization, proceeds via the same transition metal-mediated rearrangement of carbon-carbon double bonds but is applicable to α,ω-dienes, and other non-cyclic di-olefins, as opposed to the cyclic substrates employed in ROMP. Unlike its chain growth counterpart, ADMET is a step-growth polymerization process with monomers being joined end-to-end in a stepwise manner via the elimination of low molecular weight olefins (typically ethylene). Number average molecular weights ($\bar{M}_n$) are strongly dependent upon conversion as expressed by Carothers's equation.[48-50] Advanced architectures such as block copolymers are not readily accessible and dispersity values ($Đ_M = \bar{M}_w/\bar{M}_n$) generally approach a statistical distribution of 2.0.

In spite of these factors, ADMET remains an attractive technique with a level of structural precision that is unsurpassed by other systems. With judicious design of an α,ω-diene monomer, it becomes possible to position a specific functional group at a given location on the polymer backbone (*i.e.* tailored branch identity and frequency) with very few/ negligible defects.[51, 52] This is a powerful ability, particularly when combined with the broad functional group tolerance exhibited in particular by Grubbs' ruthenium-based metathesis catalysts.

Structurally precise ADMET polymers often display unique thermal and crystallization behavior[53-58] and have found application in the modelling of high volume commodity polymers such as polyethylene[58] and branched and functional variants thereof.[59-77] Precision ADMET polymers also hold great promise in drug delivery systems and the biomedical arena where the relative position of moieties can be as important as chemical identity in terms of cell recognition and binding.[78-82] The synthesis of conjugated and electro-active polymers is another prominent field, and ADMET (particularly when performed in the solid state) is well suited to preparing these intractable materials.[83-90] Finally, there is extensive literature on the use of ADMET in 'green chemistry'.[91-97] Many naturally derived olefins are suitable or can be readily transformed into suitable ADMET monomers, and as a reversible reaction, ADMET conditions may be engineered to depolymerize certain rubbers.[48]

The key challenge in preparing precision ADMET materials is the synthesis of symmetrical monomers of sufficiently high purity. There is a lack of commercially available substrates and α,ω-dienes are typically prepared using demanding multistep procedures. Herein we describe the facile synthesis of a novel symmetrical α,ω-diene bearing an acrylate functionalized central pendant. The nucleophile initiated thiol-Michael reaction of this common precursor with a range of different thiols affords ready access to a library of functional thioether-based adducts which were examined as suitable ADMET monomers. In contrast to our previous reports employing a similar approach for ROMP-active monomers,[39] it was found that the thioether moiety competitively coordinated with Grubbs' 1st generation catalyst ($RuCl_2(PCy_3)_2CHPh$) under the slower polymerization conditions associated with ADMET systems. This necessitated an additional synthetic step in which the thioether functional groups were converted to sulfones via oxidation with triazotriphosphorine tetrachloride (TAPC).[98] All oxidized species underwent (co)polymerization to high conversion, validating this approach as a convenient route to functional ADMET polymers.

Finally, we demonstrate that the carbon-carbon double bonds in the backbone of each ADMET polymer can be quantitatively modified via a radical initiated thiol-ene reaction. Residual C=C bonds are typically hydrogenated to improve oxidative stability[99-101] or to produce polyethylene analogues[58] but in this work we emphasize the potential of the thiol-ene reaction for expedient post-polymerization functionalization of ADMET polymers instilling a variety of novel functional groups.

Experimental

All reagents were purchased from the Aldrich Chemical Company and used as received unless noted otherwise.

Instrumentation

High-resolution mass spectrometry of small molecules was performed on a Bruker Bio Apex II Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS). The system was fitted with 7 Tesla magnets and an Analytica source.

^{1}H and ^{13}C NMR spectra of monomers and polymers taken at the University of Florida were acquired on a Varian Mercury 300 MHz NMR spectrometer using a 5 mm pulsed field gradient (PFG) probe. ^{1}H, ^{13}C and ^{19}F NMR spectra recorded at the University of New South Wales were acquired on a Bruker DPX 300 MHz NMR spectrometer fitted with a 5 mm double resonance broad band BBFO z-gradient probe. ^{1}H and ^{19}F spectra were averaged from 32 scans while ^{13}C were averaged over 256-1024 scans depending on sample concentration. Deuterated solvents were purified by passage through a short column of anhydrous potassium carbonate to remove trace acidity and moisture. Spectra and free induction decay (FID) Fourier transforms were processed using the Topspin software package and all data is reported as follows: chemical shift in ppm [multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet), coupling constants in Hertz, integration].

Infrared spectra were collected on a Thermo Nicolet 5700 FTIR spectrometer equipped with a single bounce diamond stage attenuated total reflectance (ATR) accessory. A resolution of 2 cm^{-1} and a spectral window of 650 to 4000 wavenumbers was chosen and spectra were accumulated from 32 averaged scans.

Size exclusion chromatography (SEC) analysis of polymer samples was performed in *N,N*-dimethylacetamide [DMAc, 0.03% w/v LiBr, 0.05% 2,6-dibutyl-4-methylphenol (BHT)] at 50°C. Sample solutions were injected into a Shimadzu modular system comprising an SIL-10AD autoinjector, a Polymer Labs (PL) 5.0 μm bead-size guard column (50 x 7.5 mm^2) followed by four linear PL Styragel columns (10^5, 10^4, 10^3 and 500Å) and an RID-10A differential refractive index detector. A flow rate of 1.0 mL min^{-1} was employed and calibration was achieved with commercial narrow molecular weight distribution polystyrene standards with $\overline{M}_n$'s ranging from 500 to 10^6 g mol^{-1}. For samples insoluble in DMAc, a similar system with THF as eluent operating at 40°C was employed.

Radical thiol-ene reactions were conducted in a 400W Rayonet RPR-200 photochemical reactor fitted with 16 x 2537Å light sources. A cylindrical reactor geometry was used (40 cm deep with a 16 cm radius), with each lamp arranged in a vertical orientation. The intensity of ultra-violet radiation at the centre of the chamber was approximately 1.65 x 10^{16} photons/sec/cm^3 and an equilibrium operating temperature of 44°C was typical. Mechanical stirring was provided via a compressed air powered magnetic stirrer and samples (loaded in UV-transparent RQV-7 and RQV-3 quartz test tubes) were suspended in the centre of the instrument.

Preparation of 11-bromoundec-1-ene (A)

A solution of 10-undecen-1-ol (100 g, 0.587 mol) and carbon tetrabromide (215.7 g, 1.1 eq. 0.650 mol) in distilled anhydrous

dichloromethane (500 mL) was prepared in a flame dried 2 L round bottom flask under Ar. A magnetic stirrer bar was inserted and the flask was cooled to 0°C in an ice bath. Triphenylphosphine (170.5 g, 1.1 eq. 0.650 mol) was then added under positive Ar pressure, in portions over 30 min. with vigorous stirring. The reaction was allowed to warm to room temperature and stirred for an additional 4 h. TLC (95:5 hexane/ ethyl acetate) was used to verify the complete consumption of starting material (R_f = 0.35) and formation of product (R_f = 0.9), before the reaction mixture was concentrated *in vacuo* to a brown oil. Hexane (1 L) was poured into the flask to precipitate white phosphorous oxide that was subsequently removed by filtration, washed thoroughly with additional hexane and discarded. The combined filtrates were concentrated *in vacuo* and fractionally distilled over CaH_2 (20 g). The first fraction (hexane) was removed at room temperature under a partial vacuum of 100 mmHg (regulated via manometer). The second fraction (bromoform, $CHBr_3$) was retrieved between 57 and 61°C at 35mmHg. After discarding the first few drops, the product 11-bromoundec-1-ene was collected at 149-150°C (35 mmHg) as a colourless oil. It was stored in a flame dried round bottom flask over activated molecular sieves (3Å) (117 g, 86% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.34 (m, 12H), 1.85 (pentet, J = 7 Hz, 2H), 2.04 (q, J = 6.5 Hz, 2H), 3.40 (t, J = 7 Hz, 2H), 4.95 (m, 2H), 5.80 (m, 1H).

Preparation of diethyl 2,2-di(undec-10-en-1-yl)malonate (B)
Diethyl malonate (50 g) was distilled over CaH_2 (5 g) and collected as a pure fraction at 75-76°C (10 mmHg). It was stored in a flame dried round bottom flask over activated molecular sieves (3Å).

A flame dried 3-neck 2 L round bottom flask was assembled under Ar with a magnetic stirrer bar, condenser and dropper funnel. Distilled anhydrous THF (600 mL) was transferred via cannula and NaH (ca. 40 g of a 60 wt% dispersion in oil, 1.0mol) was added under positive Ar pressure to form a slurry. Distilled diethyl malonate (32.6 mL, 0.214 mol) was added to the dropper funnel via cannula and was introduced to the NaH slurry in a dropwise manner over 30 min. The dropper funnel was rinsed with a small amount (20 mL) of anhydrous THF before 11-bromo-1-undecene (103.48 mL, 2.2 eq. 0.472 mol) was cannulared in. This was added dropwise (over 30 min.) with vigorous stirring and the reaction mixture was refluxed for 48 h. TLC (98:2 hexane/ ethyl acetate) was used to confirm complete consumption of diethyl malonate (R_f = 0.1) and 11-bromo-1-undecene (R_f = 0.8) as well as formation of the product (R_f = 0.4). Additional bromo alkene may be added if a significant mono-alkylated species is detected (R_f = 0.25), followed by further refluxing to promote formation of the di-alkylated product. The reaction was then cooled to 0°C in an ice bath and water was added dropwise to neutralize residual NaH. The crude (containing 2,2-di(undec-10-en-1-yl)malonate as the major product) was used without further treatment as a reagent in subsequent synthetic steps.

Preparation of 2,2-di(undec-10-en-1-yl)malonic acid (C)
Crude 2,2-di(undec-10-en-1-yl)malonate (B), NaOH pellets (60 g, 1.5 mol) and 400 mL of EtOH/ H_2O (1:1) were added to a 2 L round bottom flask. The reaction was then refluxed until complete consumption of the di-ester starting material (R_f = 0.4) as determined by TLC (98:2 hexane/ ethyl acetate). The mixture was acidified to a pH of 1 with concentrated HCl and concentrated *in vacuo* to remove residual THF and EtOH. The aqueous solution was extracted three times with Et_2O and the combined organic fractions were dried over Na_2SO_4 and filtered. *In vacuo* concentration yielded a yellow oil (containing 2,2-di(undec-10-en-1-yl)malonic acid as the major component) which was used as a reagent in subsequent synthetic steps.

Preparation of 2-(undec-10-en-1-yl)tridec-12-enoic acid (D)
A magnetic stirrer bar and 1200 mL of distilled anhydrous THF were added to a 2 L flame dried round bottom flask under Ar. 120 g of frozen crude 2,2-di(undec-10-en-1-yl)malonic acid (C) (ca. 0.290 mol) was weighed into the flask under a positive flow of Ar and allowed to dissolve. The addition of 1,1'-carbonyldiimidazole (52.4 g, 1.1 eq. 0.320 mol) caused the reaction to effervesce and it was necessary to off-gas the system via a bubbler. The mixture was stirred for 3 h. at which point TLC (90:10 hexane/ ethyl acetate) confirmed the disappearance of the di-acid starting material (R_f = 0.75) and formation of the decarboxylated carbonyl imidazole species (R_f = 0.6). 150 mL of an aqueous solution of NaOH (17.6 g, 1.5 eq. 0.44 mol) was poured into the flask to generate the carboxylate anion and the reaction was stirred for 2 h. The crude was then concentrated *in vacuo* to remove the THF before acidification with 1M HCl (1200 mL, 4 eq.) to pH < 1. After extraction with CH_2Cl_2 (3 x 300 mL), the combined organic fractions were dried over Na_2SO_4 sodium sulfate, filtered and concentrated *in vacuo* to yield an orange oil.

A large 6 L chromatography column was prepared and pure 2-(undec-10-en-1-yl)tridec-12-enoic acid (D) was isolated in three batches. A 90:10 hexane/ ethyl acetate eluent was employed and D was collected as the 6th fraction (R_f = 0.4) (38.4 g, 49% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.27 (m, 32H), 2.03 (q, J = 6.5 Hz, 4H), 2.35 (s, 1H), 4.95 (m, 4H), 5.81 (m, 2H), 10.21 (br, 1H).

Preparation of 2-(undec-10-en-1-yl)tridec-12-en-1-ol (E)
Lithium aluminium hydride (LAH) pellets (10.9 g, 3 eq. 0.288 mol), a magnetic stirrer bar and 300 mL of distilled anhydrous Et_2O were combined in a flame dried Ar-purged 1 L round bottom flask. This was stirred for 2 h. until the LAH pellets had completely disintegrated and the mixture had become a turbid grey solution. The flask was cooled to 0^{o}C in an ice bath and 35 g (0.096 mol) of frozen 2-(undec-10-en-1-yl)tridec-12-enoic acid (**D**) was added portion-wise (10 min.) under a positive pressure flow of Ar. Bubbling was observed during addition. The reaction was allowed to equilibrate to room temperature and stirring continued overnight. Distilled water was then added dropwise to quench the reaction. Upon formation of a gel, 3M HCl was used to dissolve the precipitated salts and

complete the quenching. The reaction mixture was extracted three times with Et_2O, washed once more with distilled water and dried thoroughly over MgSO4. The combined organic extracts were filtered and concentrated *in vacuo* to yield 2-(undec-10-en-1-yl)tridec-12-en-1-ol as a viscous colourless oil (31.3 g, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.27 (m, 33H), 2.03 (m, 4H), 3.48 (m, 2H), 4.95 (m, 4H), 5.82 (m, 2H).

Preparation of 2-(undec-10-en-1-yl)tridec-12-en-1-yl acrylate (F)

A solution of E (30 g, 0.086 mol) and freshly distilled Et_3N (13.1 mL, 1.1 eq. 0.094 mol) in 600 mL of anhydrous THF was prepared in a flame dried Ar-purged three neck round bottom flask fitted with a magnetic stirrer bar and dropper funnel. A second solution of freshly distilled acryloyl chloride (7.8 mL, 1.1 eq. 0.094 mol) in 20 mL of anhydrous THF was prepared in the dropper funnel. The system was then cooled to 0°C and the acryloyl chloride added to the alcohol in a drop-wise fashion over 30 min. The white suspension of ammonium salts was stirred for 3 h. at 0°C and at ambient temperature overnight. The mixture was then concentrated *in vacuo* to remove the THF before it was dissolved in brine and extracted three times with CH_2Cl_2. The organic fractions were combined, dried over MgSO4, filtered and concentrated *in vacuo* to yield 2-(undec-10-en-1-yl)tridec-12-en-1-yl acrylate (F) as a colourless oil (32.05 g, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.27 (m, 33H), 2.03 (t, J = 7.5 Hz, 4H), 4.05 (d, J = 5.6 Hz, 2H), 4.95 (m, 4H), 5.82 (m, 3H), 6.11 (m, 1H), 6.38 (d, J = 17 Hz, 1H). ^{13}C NMR (75MHz, $CDCl_3$, ppm): δ = 14.10, 22.65, 26.70, 28.94, 29.14, 29.50, 29.57, 29.92, 31.29, 33.81, 37.32, 67.30, 114.09, 128.72, 130.19, 139.10, 166.29; HRMS: calcd. for $C_{27}H_{48}O_2$ [M + $H^{+\bullet}$]: 405.3727, found: 405.3728.

Thiol-Michael coupling of small molecule thiols with 2-(undec-10-en-1-yl)tridec-12-en-1-yl acrylate (F)

1.0 g (2.47 mmol) of 2-(undec-10-en-1-yl)tridec-12-en-1-yl acrylate (F) and a thiol tX from Figure 2 (1.0 eq. 2.47 mmol) were dissolved in 5 mL of CH_2Cl_2 in a glass vial. Dimethylphenylphosphine (0.1M in CH_2Cl_2, 0.25 mL, ca. 1 mol%) was added to this solution and the reaction stirred at room temperature under a normal air atmosphere. In all instances reactions were monitored by TLC. Upon completion, solvent was removed *in vacuo* to yield the crude product. The desired thiol-Michael adducts (**FtX**) were obtained in high yield and purity by flash chromatography.

Oxidation of thiol-Michael adducts Ft1-9

2.0 mmol of thiol-Michael adduct **FtX** and 6.95 mg (0.2 mmol, 0.1 eq.) of 1,3,5-triazo-2,4,6-triphosphorine-2,2,4,4,6,6-tetrachloride were mixed in a glass vial with a magnetic stirrer bar. 0.4 mL of 30% H_2O_2 (4.0 mmol, 2 eq.) was added and the reaction mixture stirred until complete consumption of the starting material (typically 1-2 h.) as observed by TLC (90:10 hexane/ ethyl acetate). The mixture was then diluted with 20 mL of distilled water and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic fractions were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The pure oxidized thiol-Michael adducts (**OxFtX**) were obtained in high yield and purity by flash chromatography.

2-(Undec-10-en-1-yl)tridec-12-en-1-yl 3-((2,2,2-trifluoro-ethyl)sulfonyl)propanoate (OxFt1)

^{1} NMR (300MHz, $CDCl_3$, ppm): δ = 1.20 - 1.50 (br, 33H), 2.04 (q, 4H, J = 6Hz), 2.88 (t, 2H, J = 8Hz), 3.02-3.30 (m, 2H) 3.38 – 3.58 (m, 2H), 4.05 (d, 2H, J = 6Hz), 4.88 – 5.05 (m, 4H), 5.72 – 5.90 (m, 2H); ^{13}C NMR (75MHz, $CDCl_3$, ppm): δ = 26.14, 26.69, 28.94, 29.58, 30.08, 31.15, 33.81, 37.28, 48.32, 68.37, 114.10, 139.25, 171.05; ^{19}F NMR (282 MHz, $CDCl_3$, ppm): δ = -60.75; HRMS: calcd. for $C_{29}H_{51}F_3O_4S$ [M + $Na^{+\bullet}$]: 575.3352, found: 575.3341 and 559.3397 [$C_{29}H_{51}F_3O_3S$ + $Na^{+\bullet}$]. IR (neat): ν = 3080, 2977, 2919, 2851, 1725, 1642, 1470, 1427, 1391, 1356, 1312, 1253, 1230, 1182, 1131, 1077, 1039, 988, 964, 910, 874, 845, 776, 719 cm^{-1}.

2-(Undec-10-en-1-yl)tridec-12-en-1-yl 3-((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)sulfonyl)propanoate (OxFt2)

^{1} NMR (300MHz, $CDCl_3$, ppm): δ = 1.18 - 1.43 (br, 33H), 2.03 (q, 4H, J = 6Hz), 2.50-2.70 (m, 2H), 2.70-3.17 (m, 6H), 4.04 (d, 2H, J = 6Hz), 4.88 – 5.05 (m, 4H), 5.72 – 5.90 (m, 2H); ^{13}C NMR (75MHz, $CDCl_3$, ppm): δ = 21.95, 25.18, 26.69, 29.14, 29.59, 31.16, 33.81, 37.28, 43.16, 47.58, 68.27, 114.09, 139.24, 171.21; ^{19}F NMR (282 MHz, $CDCl_3$, ppm): δ = -80.72, -113.47, -121.85, -123.08, -126.08; HRMS: calcd. for $C_{37}H_{53}F_{17}O_4S$ [M + $Na^{+\bullet}$]: 939.3285, found: 939.3264 and 923.3351 [$C_{37}H_{53}F_{17}O_3S$ + $Na^{+\bullet}$]. IR (neat): ν = 3080, 2922, 2854, 1733, 1717, 1643, 1470, 1392, 1332, 1298, 1233, 1199, 1146, 1117, 1086, 1031, 991, 960, 911, 724, 706, 693 cm^{-1}.

2-(Undec-10-en-1-yl)tridec-12-en-1-yl 3-(benzylsulfonyl) propanoate (OxFt3)

^{1} NMR (300MHz, $CDCl_3$, ppm): δ = 1.04 - 1.46 (br, 33H), 2.06 (q, 4H, J = 6Hz), 2.82 (t, 2H, J = 8Hz), 3.19 (t, 2H, J = 8Hz), 4.03 (d, 2H, J = 6Hz), 4.31 (s, 2H), 4.88 – 5.05 (m, 4H), 5.72 – 5.90 (m, 2H), 7.36 – 7.56 (br, 5H); ^{13}C NMR (75MHz, $CDCl_3$, ppm): δ = 26.68, 28.94, 29.59, 31.13, 33.81, 37.25, 46.55, 60.21, 68.30, 114.10, 129.16, 130.65, 139.26, 170.58; HRMS: calcd. for $C_{34}H_{56}O_4S$ [M + $H^{+\bullet}$]: 561.3972, found: 561.3972. IR (neat): ν = 3066, 2920, 2851, 1734, 1642, 1494, 1466, 1420, 1394, 1372, 1301, 1267, 1192, 1122, 1060, 1030, 992, 904, 827, 778, 761, 739, 722, 693 cm^{-1}.

2-(Undec-10-en-1-yl)tridec-12-en-1-yl 3-(dodecylsulfonyl) propanoate (OxFt4)

^{1} NMR (300MHz, $CDCl_3$, ppm): δ = 0.90 (t, 3H, J = 6Hz), 1.03 - 1.55 (br, 51H), 1.80 – 1.93 (m, 2H), 2.06 (q, 4H, J = 6Hz), 2.89 (t, 2H, J = 8Hz), 3.01 (t, 2H, J = 8Hz), 3.30 (t, 2H, J = 8Hz), 3.55 – 3.82 (m, 2H), 4.04 (d, 2H, J = 6Hz), 4.31 (s, 2H), 4.88 – 5.05 (m, 4H), 5.72 – 5.90 (m, 2H); ^{13}C NMR (75MHz, $CDCl_3$, ppm): δ = 14.12, 21.96, 22.68, 26.69, 29.15, 29.59, 31.15, 31.90, 33.82, 37.27, 47.93, 53.53, 68.35, 114.10, 139.25,

170.70; HRMS: calcd. for $C_{39}H_{74}O_4S$ [M + $Na^{+\bullet}$]: 661.5200, found: 661.5192. IR (neat): ν = 3075, 2917, 2850, 1736, 1642, 1468, 1422, 1391, 1323, 1266, 1251, 1187, 1156, 1133, 1109, 1056, 1025, 991, 967, 906, 850, 770, 754, 719 cm^{-1}.

ADMET polymerization of oxidized thiol-Michael adducts OxFt1-4

2.0 mmol of oxidized monomer **OxFtX** was weighed into a small flame dried Schlenk tube equipped with a magnetic stirrer bar. The tube was heated to 50°C to melt the monomer (all sulfone adducts were solid at room temperature) and a long needle was inserted to bubble Ar through the liquid for 1 h. Grubbs' 1st generation catalyst (16.4 mg, 1 mol%) was then added directly to the monomer under positive Ar pressure and stirring commenced. Strong bubbling was observed as the catalyst dissolved. Once the evolution of ethylene gas began to diminish, a gradually increasing vacuum was applied until 10^{-2} mmHg was achieved. After 24 h. the polymerization was dosed with an additional 1 mol% of Grubbs' catalyst and left under full vacuum for 1 week. Note that viscosity increased significantly with conversion and that after 24 h. it was necessary to manually move the stirrer bar with a strong neodymium magnet to agitate the reaction mixture. This was done periodically over the course of the week. Reaction progress was monitored via ^{1}H NMR spectroscopy and the polymerization was quenched at high conversion by dissolving the mixture in 10 mL of an ethyl vinyl ether/ toluene solution (1% v/v). Precipitation in 1 L of acidified (1M HCl) MeOH followed by Buchner filtration afforded the target polymer.

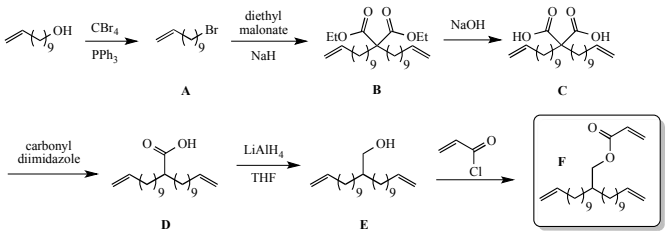
Backbone modification via a radical thiol-ene reaction

A typical procedure for the backbone modification of an ADMET polymer follows:

Poly(2-(undec-10-en-1-yl)tridec-12-en-1-yl 3-(dodecyl sulfonyl)propanoate) (poly**OxFt4**) (25.0 mg, 0.078 mmol with respect to backbone C=C bonds) was added to a quartz test tube (5 mL capacity). A 2-fold excess of thiol (**t3**) was added to the vial, along with 1 mL of CH_2Cl_2 and a magnetic stir bar. A stock solution of 2,2-dimethoxy-2-phenylacetophenone (DMPA) (10.0 mg, 50mol%, 0.039mmol) in 2.5mL of CH_2Cl_2 was prepared and a 25 μL (0.5mol%) aliquot was added to the quartz vial. The vial was then capped with a rubber septum and thoroughly sparged with N_2. After loading into a Rayonet RPR-200 photoreactor the vial was exposed to UV light (253.7 nm, $1.65x10^{16}$ photons/sec/cm^3) under stirring for 240 h. The product was precipitated twice in MeOH, centrifuged and dried *in vacuo*.

Results and Discussion

The nucleophile initiated thiol-Michael reaction is a facile process for the hydrothiolation of an electron deficient C=C bond.[16, 20, 27, 31, 102] In order to take advantage of this selectivity, we designed and synthesized the novel symmetrical α,ω-diene acrylate 2-(undec-10-en-1-yl)tridec-12-en-1-yl acrylate (**F**) shown in Scheme 1. Subsequent nucleophile-mediated Michael addition reactions on this precursor occurred exclusively at the pendant activated C=C bond, allowing for the quick and convenient generation of a wide range of new, functional ADMET monomers.



Scheme 1. Synthesis of an acrylic functional α,ω-diene, 2-(undec-10-en-1-yl)tridec-12-en-1-yl acrylate.

The basic α,ω-diene structure was prepared by the dialkylation of commercially available diethyl malonate with 11-bromo-1-undecene (**A**). Although 11-bromo-1-undecene can be purchased, the presence of isomeric impurities in the commercial sample negates the precision of ADMET polymerization. 10-Undecen-1-ol exhibits high isomeric purity and was identified as an alternative precursor. Its reaction with carbon tetrabromide and subsequent distillation yielded pure 11-bromo-1-undecene in 86% yield.

A 9,9 configuration was selected for this study because it yields a polymer with a regular spacing of 20 carbons between functional groups. Previous studies[53-58] have determined that shorter intervals between functional groups can force those pendant species to be included in a distorted crystal lattice, whereas intervals of 20 carbons or more allow functional groups to self-assemble in the amorphous region. Nevertheless, the procedure may be readily adapted to prepare monomers of different lengths. Shorter α,ω-dienes are obtained by alkylation of small halo alkenes, while longer dienes may be synthesized from 9-decen-1-ol via an iterative coupling procedure developed by the Wagener group.[103] Base catalyzed hydrolysis followed by decarboxylation yielded 2-(undec-10-en-1-yl)tridec-12-enoic acid (**D**), which was reduced with $LiAlH_4$ to the corresponding alcohol 2-(undec-10-en-1-yl)tridec-12-en-1-ol (**E**). Acylation with acryloyl chloride gave the target acrylic precursor 2-(undec-10-en-1-yl)tridec-12-en-1-yl acrylate (**F**), as a colourless oil in 92% yield. The ^{1}H NMR spectrum of **F**, recorded in $CDCl_3$ with relevant signals and integral values noted, is shown in Figure 1.

With the key substrate, **F**, in hand, a series of nucleophilic thiol-Michael additions were carried out in the presence of a catalytic amount of dimethylphenylphosphine (Scheme 2). The suite of thiols that were employed are shown in Figure 2 and included trifluoro (**t1**), perfluoro (**t2**), aromatic (**t3**), dodecyl (**t4**) and trisethoxysilane (**t5**) species. Although prior work[39] has demonstrated the broad range of functionalities compatible with this chemistry, more polar functionalities were avoided in

this proof-of-concept study due to solubility issues with the relatively hydrophobic α,ω-diene.

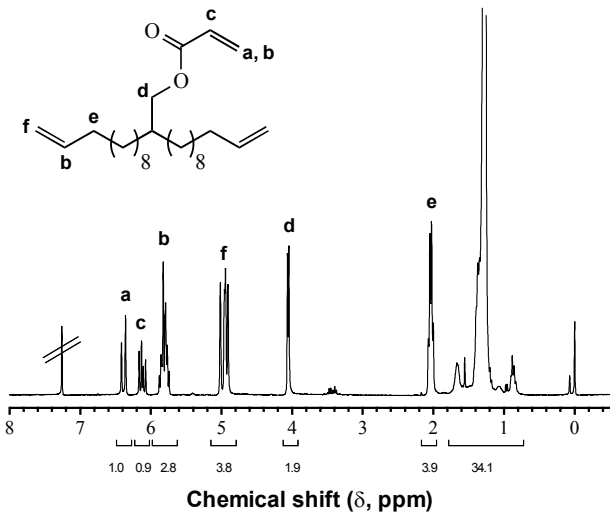
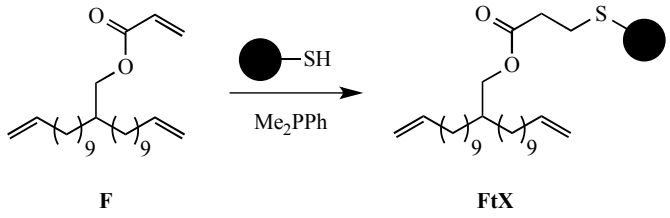


Figure 1. ^{1}H NMR spectrum of 2-(undec-10-en-1-yl)tridec-12-en-1-yl acrylate (**F**), recorded in $CDCl_3$.



Scheme 2. Synthesis of thioether functional α,ω-dienes via phosphine-mediated thiol-Michael conjugation

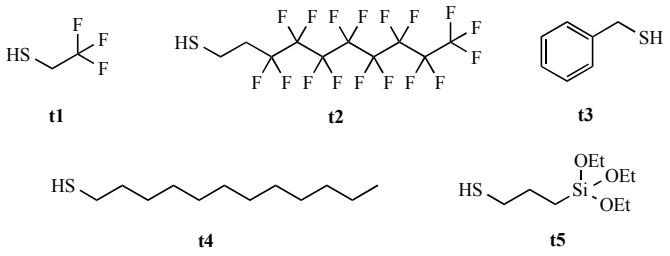


Figure 2. Group of thiols conjugated to the acrylic α,ω-diene precursor (F)

Thiol-Michael conjugation between **F** and each thiol was successful and the corresponding thioether adducts (**Ft1-5**) were obtained in essentially quantitative yield. A representative ^{1}H NMR spectrum, of the triethoxysilane functionalized adduct 2-(undec-10-en-1-yl)tridec-12-en-1-yl 3-((3-(triethoxysilyl)-propyl)thio)propanoate (**Ft5**), is given in Figure 3.

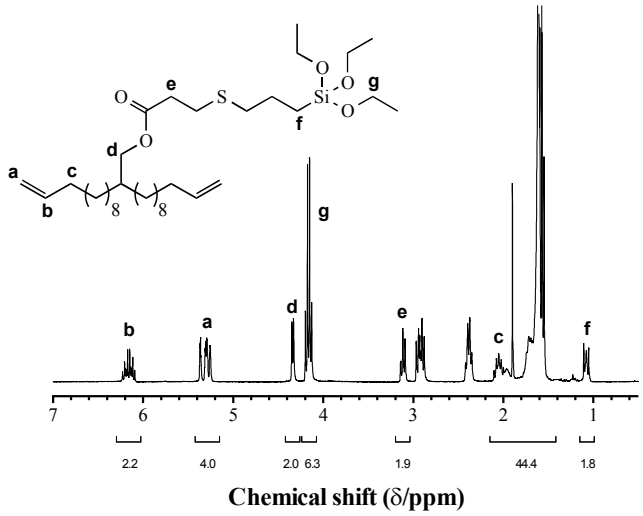


Figure 3. ^{1}H NMR spectrum 2-(undec-10-en-1-yl)tridec-12-en-1-yl 3-((3-(triethoxysilyl)propyl)thio)propanoate (Ft5), recorded in $CDCl_3$, with key signals and their respective integral values highlighted

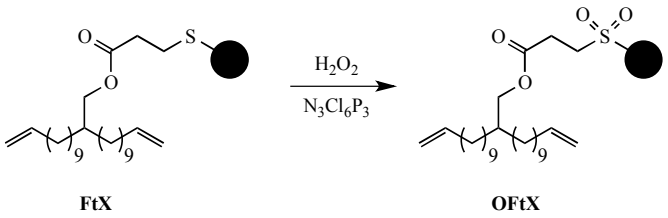
The absence of any signals associated with the acrylic functionality and the appearance of signals such as those labelled **f** and **g** associated with the siloxy species confirm successful adduct formation.

In our previous studies with ROMP-active *exo*-7-oxanorbornene substrates we demonstrated that such thioether adducts were readily accessible under facile conditions and that they could be (co)polymerized with the Grubbs' first generation initiator, $RuCl_2(PCy_3)_2CHPh$, highlighting that ROMP, at least, is tolerant of thioether functionality.[38-41] Given this, we initially examined the direct ADMET polymerization of 2-(undec-10-en-1-yl)tridec-12-en-1-yl 2-(benzylthio)acetate (**Ft3**). The benzyl derivative was chosen since the aromatic pendant group is relatively inert and non-coordinating. The general ADMET procedure described in the experimental section was followed. However, apart from an initial brief period of activity, no effervescence or increase in viscosity was observed. Monomer conversion remained low, even after the addition of a further 5 mol% catalyst, and only short oligomers were detected after 1 week of 'polymerization'.

This poor result was unexpected since the *exo*-7-oxanorbornene benzyl analogue of **Ft3**[39] was found to undergo successful and controlled ROMP using the same $RuCl_2(PCy_3)_2CHPh$ initiator. Further examination of these new ADMET thioether-based monomers confirmed that none of the adducts could be effectively homopolymerized and it was hypothesized that under the much slower polymerization conditions associated with ADMET that the nucleophilic thioether moiety was, in fact, coordinating with the electrophilic ruthenium metal centre forming a mono-chelate

structure similar to latent metathesis catalysts reported in the literature.[104]

While highly active Schrock species were considered as potential alternative catalysts/initiators, their incompatibility with oxygen (present in the ester groups) precluded their use. Additionally, the more active 2nd and 3rd generation Grubbs' catalysts were also considered, but while they may have achieved higher conversions prior to deactivation, they were expected to ultimately undergo the same sulfur coordination at their Ru core. Furthermore, their use in precision ADMET systems is generally discouraged due to their propensity towards olefin isomerization. Instead, an approach involving chemical modification of the thioether was examined, and specifically, conversion of the thioether functionality to a chemically inert sulfone employing triazotriphosphorine tetrachloride (TAPC) as the oxidizing agent, Scheme 3.



Scheme 3: Protective oxidation of a thioether to a sulfone moiety

The TAPC oxidation of sulfur is a rapid, quantitative and generally chemoselective process.[98] A representative ^{1}H NMR spectrum of the oxidized benzyl functionalized monomer (**OxFt3**) is shown in Figure 4. The spectrum is entirely consistent with the expected structure of the sulfone derivative. However, two problems were encountered with this general oxidation approach. Firstly, due to the *in situ* generation of hydrochloric acid the trisethoxysilane adduct (**Ft5**) underwent hydrolysis and condensation during oxidation, resulting in the formation of an intractable gel, and as such was not examined further. Secondly, the extremely hydrophobic fluorinated adducts **Ft1** and **Ft2** were difficult to oxidize in the aqueous reaction environment. Vigorous stirring and extended reaction times were required before the starting material was consumed as judged by TLC. High-resolution mass spectrometry (see experimental section) and examination of the post-workup ^{1}H NMR spectra (see supporting information) revealed that the fluorinated precursor thioether adducts only underwent partial oxidation resulting in a mixture of both sulfoxide (predominant species) and sulfone.

Since the benzyl and dodecyl thioether adducts were both quantitatively converted to the corresponding sulfones (**OxFt3** and **OxFt4** respectively) we initially examined these two substrates in ADMET homopolymerizations. ADMET homopolymerization of **OxFt3** and **OxFt4** proceeded smoothly and the evolution of ethylene gas was observed up to 2 weeks after the addition of $RuCl_2(PCy_3)_2CHPh$. All of the oxidized monomers exhibited melting points slightly above room temperature and were homopolymerized under bulk conditions to facilitate removal of ethylene from the system, enhance kinetics and minimize secondary intramolecular metathesis events. As a representative example, the ^{1}H NMR spectrum, recorded in $CDCl_3$, of the homopolymer obtained from the oxidized benzyl sulfonyl adduct (poly(**OxFt3**)) is given in Figure 5, while the experimentally determined molecular weight distributions for poly(**OxFt3**) and poly(**OxFt4**) are shown in Figure 6.

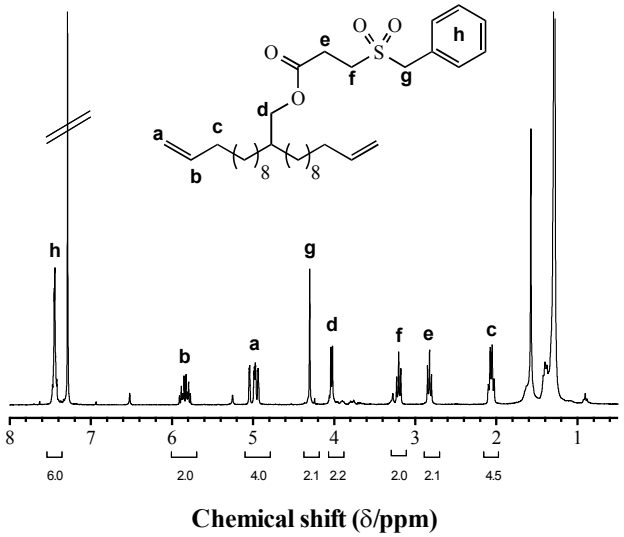


Figure 4: ^{1}H NMR of 2-(undec-10-en-1-yl)tridec-12-en-1-yl 3-(benzylsulfonyl)propanoate (OxFt3), recorded in $CDCl_3$

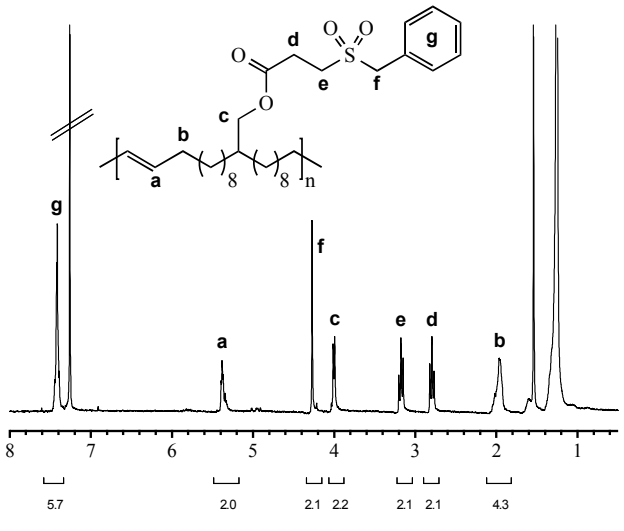


Figure 5. ^{1}H NMR spectrum of poly(2-(undec-10-en-1-yl)tridec-12-en-1-yl 3-(benzylsulfonyl)propanoate) (poly**OxFt3**), recorded in $CDCl_3$.

The ^{1}H NMR spectrum of poly(**OxFt3**) is entirely consistent with a polymeric species. The key difference between the monomer and its corresponding homopolymer is most clearly evident in the vinylic region of the spectrum. In the case of the monomer (Figure 4) we observe two sets of distinct resonances associated with the terminal monosubstituted enes. After

polymerization these signals 'merge' into essentially a single resonance observed at δ = ~5.4 ppm associated with the backbone internal ene functional groups.

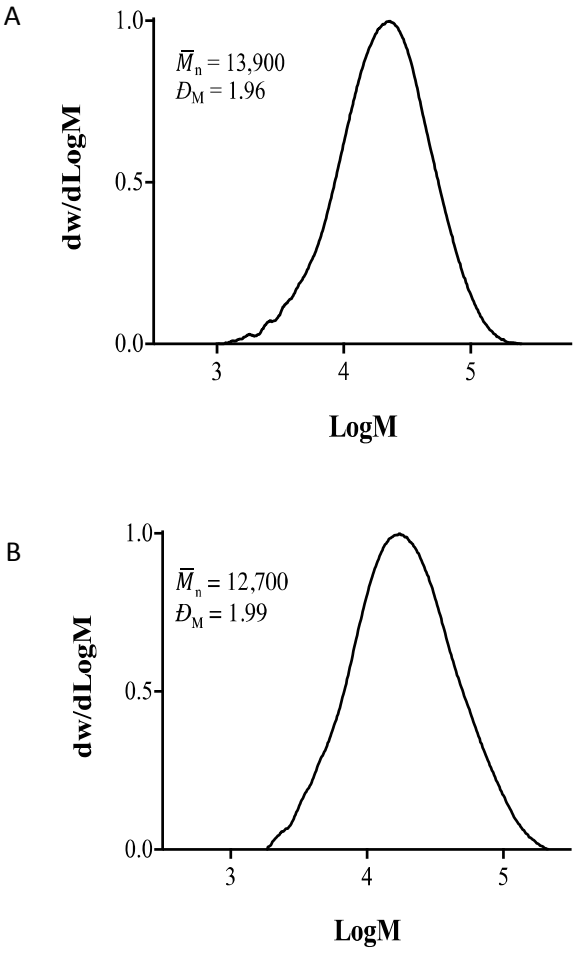


Figure 6. THF molecular weight distributions of (A) poly(2-(undec-10-en-1-yl)tridec-12-en-1-yl 3-(benzylsulfonyl)propanoate) (poly**OxFt3**) and (B) poly(2-(undec-10-en-1-yl)tridec-12-en-1-yl 3-(dodecylsulfonyl)propanoate) (poly**OxFt4**)

With respect to SEC analysis of the two homopolymers, the measured dispersities ($Đ_M$) of 1.96 and 1.99 are close to the ideal theoretical value of 2.0 for a model ADMET system, while the molecular weights of 13,900 and 12,700 are consistent with laboratory scale polymerizations that are limited by inefficient mixing at high viscosity.

^{1}H and ^{13}C NMR spectra as well as SEC-measured molecular weight distributions have been included in the supporting information while polymer properties for each of the polymerized oxidized adducts are summarized in Table 1.

As noted, the oxidized adducts **OxFt3** and **OxFt4** homopolymerized well under bulk conditions with $RuCl_2(PCy_3)_2CHPh$ as initiator. In contrast, the oxidized fluorinated derivatives, **OxFt1** and **OxFt2**, while active, yielded homopolymers of significantly lower molecular weight. This could be due to a simple hydrodynamic volume effect with the molecular weights reported in Table 1 being polystyrene equivalents. Alternatively, we reiterate that both **OxFt1** and **OxFt2** contained both sulfoxide and sulfone oxidized species as determined by mass spectrometry. While the latter is completely inert towards the Ru metal centre, as demonstrated

here is still the possibility of Ru
lfoxide species. As such, while
ized fluoro derivatives does proceed
tor deactivation over the course of a
h that attainable molecular weights
reclude the described approach as a
ssing fluoro functional ADMET
hts the need for perhaps identifying
ts/conditions for a given functional

d adducts, the parent thiols and the number
ispersities, as determined by SEC, for the

Adduct	Thiol	$\bar{M}_n$[a]	$\bar{M}_w$[a]	$Đ_M$[a]
		4,200	8,600	2.04
		2,700	(-)[c]	(-)[c]
		3,900	27,300	1.96
		2,700	25,300	1.99

with molecular weights reported as
ular weight distribution was assumed
e peak maxima ($\bar{M}_p$). c. Dispersity and
ak convolution at low molecular weight.

trated the principle of applying
nistry for the preparation of
al thioether-based ADMET monomers, we subsequently expanded our study to build upon our previous work with ROMP systems[42] with the intent of demonstrating how the radical initiated thiol-ene reaction may be employed for backbone modification of internal C=C bonds. A second suite of thiols was selected, including: benzyl mercaptan (**t3**), 2-mercaptoethanol (**t6**), an acetyl protected sugar (**t7**) and the polyhedral oligomeric silsesquioxane (POSS) (**t8**) species, Figure 7.

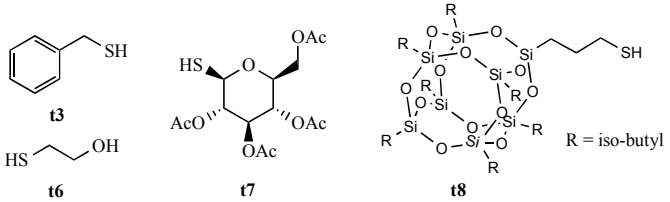


Figure 7. Thiols used for radical thiol-ene backbone modification of ADMET polymers

Initially, we focused on the backbone modification employing benzyl mercaptan, **t3**. Each polymer (poly(**OxFt1**) – poly(**OxFt4**)) was reacted with a 2-fold excess of **t3** in the presence of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA). Reactions were performed in a Rayonet UV reactor. Conversion was determined by monitoring the disappearance of the peak at δ = 5.4 ppm in ^{1}H NMR spectra, associated with the vinyl backbone H's, in periodically withdrawn aliquots. In contrast to our previously reported study with ROMP (co)polymers,[42] we found it necessary to re-dose an additional equivalent of **t3** at 120 h and 200 h. While the thiol-ene modification of the ADMET polymer backbone proved to be considerably slower and require a higher relative concentration of thiol compared to our ROMP system, quantitative backbone hydrothiolation could be achieved within 240 h. Figure 8 shows a comparison of the ^{1}H NMR spectra of poly(**OxFt4**) before and after radical thiol-ene modification with **t3** plotted between δ = 8-4.5 pm. There are several key features worth highlighting. Most importantly, we observe essentially the complete absence of the signal at δ = 5.4 ppm associated with the backbone ene after the 240 h time period. Additionally, signals attributed to the allylic H's in the parent homopolymer also completely disappear (not shown). Finally a large signal appears centred at ca. δ = 7.3 ppm associated with the newly introduced aromatic groups.

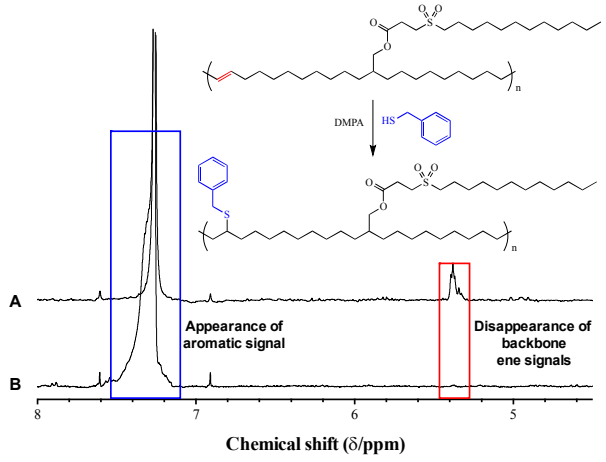


Figure 8: ^{1}H NMR spectra of poly(2-(undec-10-en-1-yl)tridec-12-en-1-yl 3-(dodecylsulfonyl)propanoate) (Poly**OxFt4**) before (A) and after (B) thiol-ene modification with benzyl mercaptan (t3), taken in $CDCl_3$.

Figure 9 shows the molecular weight distributions of poly**OxFt4** before and after modification with **t3**. After thiol-ene modification the distribution shifts to a higher average molecular weight and the dispersity increases slightly from 1.99 to 2.05. We do note, however, that such prolonged exposure to UV irradiation might result in occurrences of polymer chain cleavage and crosslinking. Such events may account for the slight broadening of the molecular weight distribution and the appearance of both higher and lower molecular weight species.

Finally, 3 samples of poly**OxFt4** were modified with **t6**, 1-thio-β-D-glucose tetraacetate (**t7**) and mercaptopropylisobutyl-POSS® (**t8**) to highlight the variety of functional groups that may be conjugated by the radical thiol-ene process. While the somewhat amphiphilic nature of these materials complicated characterization, ^{1}H NMR spectroscopy did confirm quantitative conversion as evidenced by the consumption of the backbone ene signal at δ = 5.4 ppm (see Supporting Information).

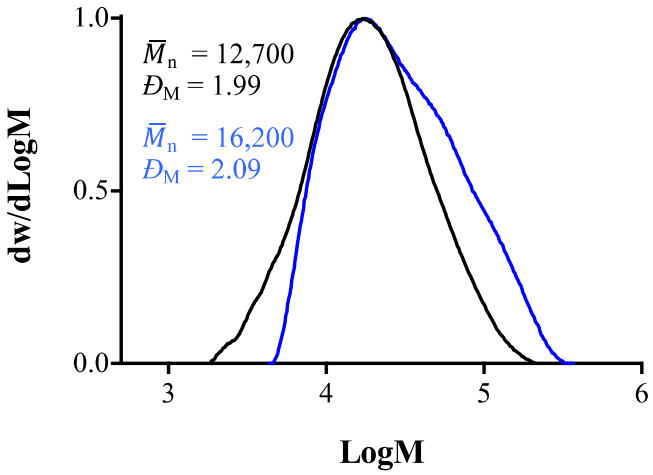


Figure 9: Molecular weight distributions of poly(2-(undec-10-en-1-yl)tridec-12-en-1-yl 3-(dodecylsulfonyl)propanoate) (poly**OxFt4**) before (block) (blue) and after thiol-ene modification with benzyl mercaptan (**t3**).

Table 2: Summary of thiol-ene backbone modification reactions performed on ADMET substrates

Polymer	Thiol	Before modification		Conv.	After modification	
		$\bar{M}_n$ [a]	$Đ_M$ [a]		$\bar{M}_n$ [a]	$Đ_M$ [a]
poly**OxFt1**	**t3**	4,200	2.04	~100	6,300[b]	(-)[c]
poly**OxFt2**	**t3**	2,700	(-)[c]	~100	4,500[b]	(-)[c]
poly**OxFt3**	**t3**	13,900	1.96	>95	16,400	2.01
poly**OxFt4**	**t3**	12,700	1.99	~100	16,200	2.05
poly**OxFt4**	**t6**	12,700	1.99	>95	12,900	1.84
poly**OxFt4**	**t7**	12,700	1.99	~100	18,800	2.08
poly**OxFt4**	**t8**	12,700	1.99	~100	20,300	1.87

a. As determined via THF SEC with molecular weights reported as polystyrene equivalents. b. Molecular weight distribution was assumed symmetrical and $\bar{M}_n$ estimated as the peak maxima ($\bar{M}_p$). c. Dispersity and $\bar{M}_w$ could not be calculated due to peak convolution at low molecular weight.

Conclusions

A novel acrylate-containing symmetrical α,ω-diene 2-(undec-10-en-1-yl)tridec-12-en-1-yl acrylate (**F**) was prepared and used

as a common substrate for the convenient preparation of a range of functional ADMET-active monomers via thiol-Michael coupling chemistry. Under typical ADMET conditions it was determined that the unprotected thioether adducts were incompatible with Grubbs' 1st generation catalyst ($RuCl_2(PCy_3)_2CHPh$) resulting in no polymerization. However, chemoselective oxidation with triazotriphosphorine tetrachloride (TAPC) readily converted the thioether to sulfoxide or sulfone moieties. These oxidized species were compatible with $RuCl_2(PCy_3)_2CHPh$ and homopolymerizations were readily accomplished to high conversion. The subsequent radical initiated thiol-ene modification of the backbone C=C bonds in the ADMET homopolymers with a selection of different functional thiols in a quantitative manner is also reported. These results highlight the compatibility and potential of thiol-based click chemistries with ADMET polymerization systems for the facile preparation of new and interesting materials.

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Notes and references

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Electronic Supplementary Information (ESI) available: Additional ^{1}H, ^{13}C and ^{19}F NMR spectra, SEC traces and mass spectrometry and FTIR data are supplied in the supporting information See DOI: 10.1039/b000000x/

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