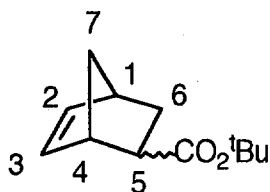


## Supplementary Material

### Preparation of 5-*t*-butylester norborn-2-ene

To a freshly cracked cyclopentadiene (10 mmol) in dry toluene (10 ml, 1M), *t*-butyl acrylate (1 equiv) was added. After leaving the reaction overnight at 170°C in a sealed ampule the reaction mixture was purified by flash chromatography on silica (0-10% Ether / *n*-Hexane) to give the product as a 1: 2 *exo* and *endo* mixture in 81% yield.



$^1\text{H NMR}$  data: (250 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$  1.28-1.36 (m, br, 3H, H6 and H7<sup>syn</sup>),  $\delta$  1.34 (s, 9H, <sup>*t*</sup>Bu),  $\delta$  1.86-1.88 (m, br, 1H, H7<sup>anti</sup>)  $\delta$  2.11 (m, 1H, H5(*exo*)),  $\delta$  2.69 (m, br, 2H, H5(*endo*) and H1),  $\delta$  2.98 (s, br, 1H, H4 (*exo*)),  $\delta$  3.15 (s, br, 1H, H4(*endo*)),  $\delta$  5.92 (dd,  $^3J_{\text{H3H2}}=5.66$ ,  $^3J_{\text{H3H4}}=3.03$ , 1H, H3(*endo*)),  $\delta$  6.10 (s, 2H, H2 and H3(*exo*)),  $\delta$  6.18 (dd,  $^3J_{\text{H2H3}}=5.67$ ,  $^3J_{\text{H2H1}}=2.81$ , 1H, H2(*endo*)).

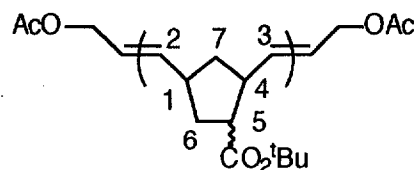
$^{13}\text{C NMR}$  data: (63 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$  28.1 (C-*Me*<sub>3</sub>), 28.9, 42.6, 44.2, 45.9, 49.6, 79.8 (C-*Me*<sub>3</sub>), 132.1 and 137.6 (C=C), 174.0 (C=O).

### A typical procedure for "pulsed addition" end-group controlled ROMP

All the polymerisation reactions were performed in a nitrogen-filled glove box. 100 equiv of 5-*t*-butylester norborn-2-ene (194 mg) in dry  $\text{CH}_2\text{Cl}_2$  (0.5 ml) was added to a stirring mixture of  $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHCH}_2\text{OAc})$  (8.2 mg, 1 equiv) and 1,4-bis-(acetox)-*cis*-but-2-ene (17.2 mg, 20 equiv) in  $\text{CH}_2\text{Cl}_2$  (1 ml). The monomer was added in 8 separate batches with 5h intervals between each addition. The reaction mixture was then poured into acidified methanol (200 ml) and the precipitate was isolated and washed several times with methanol. After drying the polymer *in vacuo*

(50°C) overnight, the acetoxy end-functionalised polynorbornene bound was obtained in 77-84% yield.

The  $^1\text{H}$  NMR spectrum of this product is shown in Fig 1.



$^1\text{H}$  NMR data:  $\delta$  1.3 (s, 9H, tBu),  $\delta$  1.5-2.0 (m, br, 4H, H6 and H7),  $\delta$  2.2-3.0 (m, br, 3H, H1, H4 and H5),

$\delta$  4.51 (m,  $\text{AcOCH}_2$ ),  $\delta$  5.2-5.4 (br,  $=\text{CH}$ ).

$^{13}\text{C}$  NMR data:  $\delta$  28.3 (C- $\text{Me}_3$ ), several peaks between 32.0 and 48.9 (CH and  $\text{CH}_2$ ), 79.9 (C- $\text{Me}_3$ ), several peaks between 128.4 and 134.4 (C=C), 174.1 (C=O).

GPC: 50 mer  $M_n$  13,900 ( $M_n(\text{calc}) = 9,800$ ),  $M_w$  20,200, Pdi 1.45. 100 mer  $M_n$  of 25,000 ( $M_n(\text{calc}) = 19,600$ ),  $M_w$  34,000, Pdi 1.38.

#### *A typical procedure for conversion of acetoxy to hydroxy end-groups*

200 mg of the acetoxy end-functionalised poly(5-*t*-butylester norbornene) was dissolved in THF (10 ml).  $\text{K}_2\text{CO}_3$  (68 mg, 5 equiv) in methanol (4 ml) was added to the mixture and the reaction was stirred for 17h. The reaction mixture was then poured into acidified methanol and the resulting precipitate was isolated and washed several times with methanol. After drying the white polymer *in vacuo* overnight at 50°C, hydroxy-end-functionalised poly(norbornene) was obtained in good yield (77 %).

$^1\text{H}$  NMR data:  $\delta$  4.08 (m,  $\text{HOCH}_2\text{C}=\text{}$ ),  $\delta$  5.1-5.6 (br, C=C).

$^{13}\text{C}$  NMR data:  $\delta$  28.2 (C- $\text{Me}_3$ ), several peaks between 32.0 and 50.5 (CH and  $\text{CH}_2$ ), 79.9 (C- $\text{Me}_3$ ), several peaks between 129.6 and 133.7 (C=C), 175.2 (C=O).

#### *Typical hydrogenation procedure*

*p*-Toluenesulfonehydrazide (5 equiv by weight) was added to a stirring mixture of the hydroxy end-functionalised poly(5-*t*-butylester norbornene) (200 mg) dissolved

in dry toluene (10 ml) in a sealed ampule. The temperature was raised to 110°C to give a translucent solution and maintained at this temperature for 17h. The reaction mixture was then allowed to cool and poured into acidified methanol. The resulting precipitate was isolated and washed several times with methanol. After drying the white polymer *in vacuo* overnight at 50°C, the hydroxy end-functionalised polynorbornane was isolated in 85 % yield.

The  $^1\text{H}$  NMR spectrum of the product poly(5-*t*-butylester norbornane) is shown in Fig 2.

$^1\text{H}$  NMR data:  $\delta$  3.64 (m,  $\text{HOCH}_2\text{CH}_2$ ), no olefinic resonances.

$^{13}\text{C}$  NMR data:  $\delta$  28.2 (C- $\text{Me}_3$ ), several peaks between 34.1 and 44.7 (CH and  $\text{CH}_2$ ), 79.6 (C- $\text{Me}_3$ ), 176.3 (C=O).

GPC of 100mer,  $M_n$  25,600,  $M_w$  33,800, Pdi 1.32.

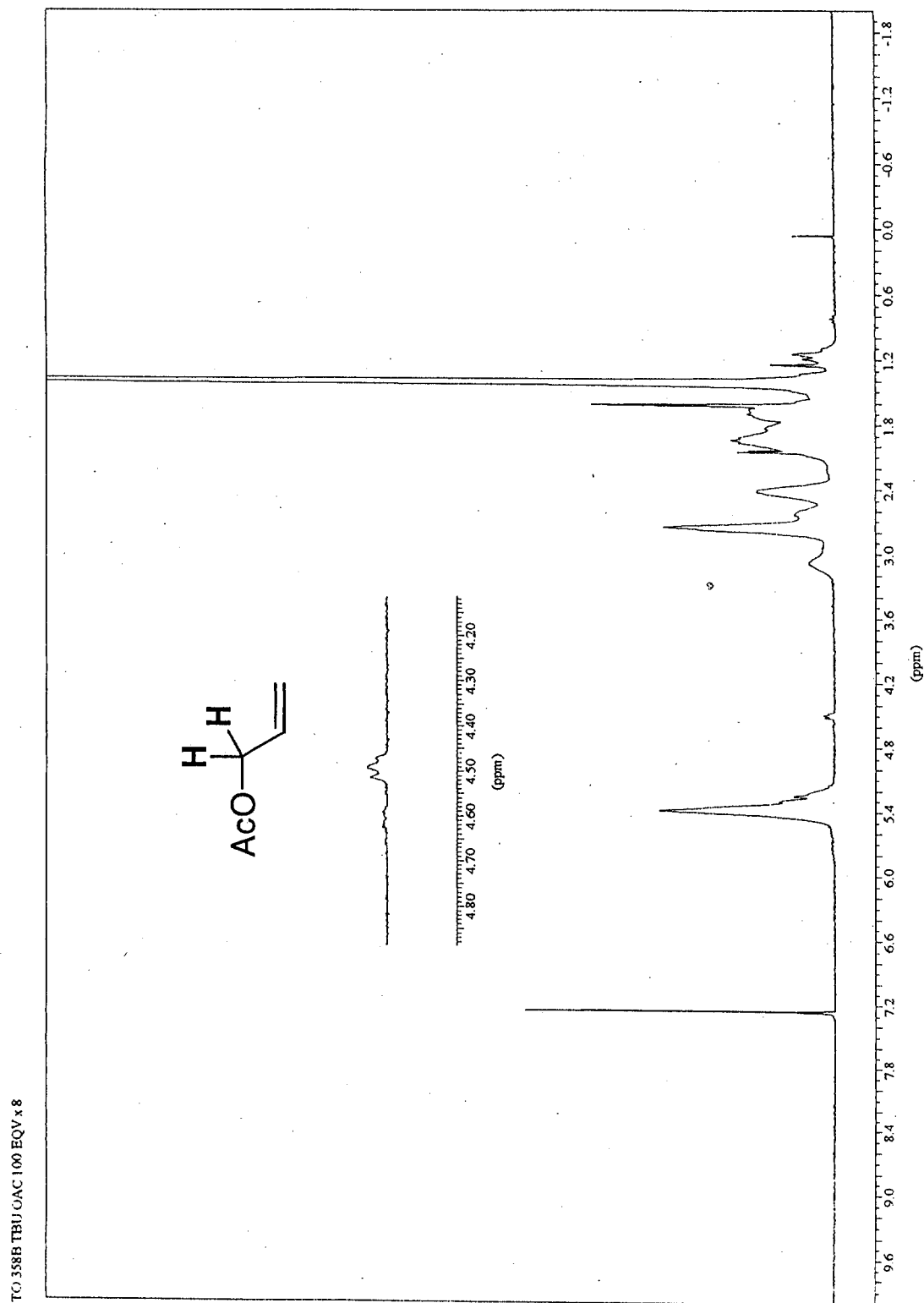
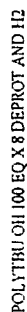


Fig 1



**Fig 2**